

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Conf. No.: **6496**

DE KROON et al

Atty. Ref.: **4662-254**

Serial No. **10/511,344**

Group: **1796**

Filed: **May 23, 2005**

Examiner: **HAIDER**

For: **MULTILAYER BLOWN FILM AND PROCESS FOR PRODUCTION THEREOF**

* * * * *

April 8, 2010

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPLICANTS' BRIEF ON APPEAL

Sir:

This Appeal is from the Official Action dated October 6, 2009, rejecting claims 1, 5 and 8-29, all of the claims presently pending herein.¹ As will become evident from the following discussion, the Examiner's rejections are in error and, as such, reversal of the same is solicited.

¹ The claims pending in this application and on appeal herein appear in the Section VIII Claims Appendix accompanying this Brief.

DE KROON et al
Serial No. 10/511,344
April 8, 2010

I. Real Party In Interest

The real party in interest is the owner of the subject application, namely DSM IP Assets B.V.

DE KROON et al
Serial No. 10/511,344
April 8, 2010

II. Related Appeals and Interferences

No appeals and/or interferences related to this application are pending.

III. Status of Claims

- A. The following claims are presently pending in this application: Claims 1, 5 and 8-29.
- B. The following claims are the claims on appeal and have been rejected in the Examiner's Official Action of October 6, 2009: Claims 1, 5 and 8-29.
- C. The following claims have been cancelled during prosecution to date: Claims 2-4 and 6-7.
- D. The following claims have been allowed: None
- E. The following claims have been withdrawn: None
- F. The following claims have been objected to: None

DE KROON et al
Serial No. 10/511,344
April 8, 2010

IV. Status of Amendments

No amendments subsequent to the October 6, 2009 Official Action have been filed.

V. Summary of Claimed Subject Matter²

The invention as defined by independent claim 1 is directed toward a process for producing a multilayer film (page 1, lines 6-7) comprised of a polyamide layer (page 1, line 7) and a polyolefin layer (page 1, line 7), the process comprising forming by blown-film processing a multilayer film containing at least a branched polyamide layer (page 1, lines 26-27) and a polyolefin layer directly connected to the polyamide layer or connected to the polyamide layer by an adhesive layer (page 4, lines 14-17), wherein said branched polyamide layer consists of a branched polyamide (page 3, lines 1-3), and said polyolefin layer consists essentially of polypropylene (page 3, lines 4-7) or LLDPE containing at most 5% of another polyethylene (page 3, lines 18-21).

The invention as defined by independent claim 5 is directed toward a multilayer film formed by blown-film processing (page 1, lines 6-7) comprising at least a polyamide layer (page 1, line 7) and a polyolefin layer (page 1, line 7) directly connected to the polyamide layer or connected to the polyamide layer by an adhesive layer (page 4, lines 14-17), wherein the polyamide layer consists of a branched polyamide (page 3, lines 1-3), and wherein the polyolefin layer consists essentially of polypropylene (page 3, lines 4-7) or of polyethylene (page 3, lines 4-7), which polyethylene layer, other than the adhesive layer, if present, contain only polyethylene which is at least 95% linear low-density polyethylene (page 3, lines 18-21).

The invention as defined by independent claim 26 is directed toward a process for producing a multilayer film (page 1, lines 6-7) comprising forming by blown-film processing a multilayer film comprising outer polyolefin layers and an intermediate polyamide layer (page 5, line 36 through page 6, line 3), wherein the outer polyolefin layers consist of a linear low density polyethylene (LLDPE), 0-10 wt.% of a polyethylene other than LLDPE, and optionally between 10 to 50 wt.% of a modified LLDPE as an

² The numbers in parenthesis refer to page and line numbers of the Substitute Specification filed on July 27, 2009 which provide representative descriptive support for the claimed subject matter.

adhesion modifier (page 3, lines 28-36), and wherein the polyamide layer consists of a branched polyamide layer (page 3, lines 1-3).

The invention as defined by independent claim 28 is directed toward a multilayer blown-film (page 1, lines 6-7) comprising outer polyolefin layers and an intermediate polyamide layer (page 5, line 36 through page 6, line 3), wherein the outer polyolefin layers consist of a linear low density polyethylene (LLDPE), 0-10 wt.% of a polyethylene other than LLDPE, and optionally between 10 to 50 wt.% of a modified LLDPE as an adhesion modifier (page 3, lines 28-36), and wherein the polyamide layer consists of a branched polyamide layer (page 3, lines 1-3).

VI. Grounds of Rejection to be Reviewed on Appeal

The following rejections to be reviewed on appeal were advanced in the Official Action dated October 6, 2009:

- (1) "Claims 1, 5, 8, 18, 12-17, 22-25 [are] rejected under 35 USC 103(a) as being unpatentable over Joachimi et al (WO 2000/39192)³ in view of Hofmann (US 3,798,115)." (Official Action dated October 6, 2009 at page 2, numbered paragraph 3.)
- (2) "Claims 1, 5, 9-11, 19-21, 26 and 28 are rejected under 35 USC 103(a) as being unpatentable over Joachimi et al (WO 2000/39192) in view of Ramesh (US 5,866,214)." (Official Action dated October 6, 2009 at page 3, numbered paragraph 8.)
- (3) "Claims 27 and 29 are rejected under 35 USC 103(a) as being unpatentable over Joachimi et al (WO 2000/39192) in view of Ramesh (US 5,866,214) and further in view of Dobreski et al (US 5,290,866)." (Official Action dated October 6, 2009 at page 4, numbered paragraph 10.)

³ US 6,566,486 is employed by the Examiner as an English-language translation.

VII. Arguments

1. Claims 1, 5, 8, 18, 12-17, 22-25 are patentably unobvious under 35 USC 103(a) over Joachimi et al in view of Hofmann

At the outset, the Examiner's attention is directed to the Supplemental Declaration under Rule 132 submitted by the inventors which clarifies the terminology to describe the processing techniques of the present invention and the multilayer film formed thereby. Such clarifications along with the amendments made to the specification by way of the Substitute Specification presented herewith present the claimed invention in a light that underscores the *unobviousness* of the same.

In this regard, as was originally described in the specification, one problem attendant with blown-film processing techniques is that when attempts were previously made to form multilayer films having layers of polyamide and polyolefin, the throughput of the blown-film system must be maintained within very narrow limits rendering the process difficult to control. This difficulty further manifests itself in terms of relatively low production rate and blow-up ratios of the bubble. In order to address this problem, the art has added a layer of low density polyethylene (LDPE) as a means to promote bubble stability but such an additional layer technically complicates the process and is more costly.

Surprisingly, the present applicants have discovered that higher throughputs with good bubble stability can be achieved for blown-film processing if a branched polyamide is employed instead of a linear polyamide. In particularly preferred embodiments, the multilayer film will be formed of outer layers which consist essentially of linear low density polyethylene (LLDPE) (i.e., contain at most 10 wt.% of a polyethylene other than LLDPE) and an intermediate layer which consists of a branched polyamide.

The Declaration evidence of record is quite instructive as to the *unobviousness* of the present invention. In this regard, the process against which the present invention

should be compared is therefore one which produces a film in which a non-branched polyamide is used with an LLDPE layer, as is exemplified in Comparative Experiment C on page 6 of the present application. As the Examiner will observe, no stable bubble could be obtained. This means therefore that the example according to the present invention (with a blow-up ratio of 2.5) should be compared to the situation where no stable bubble could be obtained.

As noted previously, one known solution to the problem to obtain a stable bubble of a film having a non-branched polyamide and an LLDPE layer is to add LDPE. This known proposal in the art is exemplified in Comparative Example A on page 6 of the present application in which a PE layer consisting of 60 wt.% LLDPE, 30wt% LDPE and 10wt.% YPAREX™ 0H040 (an MZA-modified LLDPE) together with a non-branched polyamide was employed. As noted, the blow-up ratio was only 2.1.

The present invention of course is a completely novel and unobvious solution to lack of bubble stability of a polyamide and an LLDPE layer as compared to that known in the art. In this regard, the process of the present invention results in a higher blow-up ratio of 2.5. Such an increase in blow-up ratio is in fact technically significant.

In this regard, attention is specifically directed to the article of Kim et al, Polymer Engineering and Science, 2004, vol. 44, no. 2 pages 283-302 of record herein. The Kim et al article is just one example wherein blow-up ratios are generally known in the art to be in the range from 0.5 to 3.0 as shown in Fig. 2 on page 286 and also written on page 287, right column. There it is stated that:

"The operating window for [the blow-up ratio] BUR was from 0.5 to 2.5 this range is slightly narrower than the typical BUR of 3 discussed in the literature."

Also, it will be observed fig. 2 on page 286 that the error bars for blow-up ratios are shown which demonstrate that a difference in blow-up ratio of 0.4 is fact absolutely significant.

Another example of blow-up ratios can be found in the Kirk-Othmar Encyclopedia of Chemical Technology, "Film and Sheet Materials", 3.1.1 Blown Film, of record herein. There it is noted that page 15 that the "tube is expanded by air to two or three times its diameter." From this statement it therefore follows that the blow-up ratio usually is between 2 and 3, and thus a difference of 0.4 is most certainly a technically significant advance in the art.

Turning attention to the applied publications of record, applicants note that Joachimi et al indeed mentions blown film extrusion method (column 6, line 3) as a suitable processing technique. However, the preferred method is stated as being injection molding, extrusion or extrusion blow molding (column 6, lines 6 and 7). This does not include blown film extrusion, which is a distinctly separate technique in this art as evidenced by the factual Declarations of record. Thus, Joachimi does not relate to a process for preparing blown film and problems associated therewith, let alone that branched polyamide results in higher processing rates and blow-up ratio.

Hofmann describes a three layer film, in which the outer layer is a mixture of high-viscosity polypropylene and low-viscosity polypropylene, an inner layer a mixture of polypropylene and polyamide and an outer layer of polyamide. As has been mentioned in the present application (page 1, lines 19 and 20) and mentioned briefly above, a known solution to the problem of obtaining multilayer film is to admix, particularly in the polyolefin, a material that improves processability in a blown film process. This known prior art technique is exactly what has been described in Hofmann.

Moreover, in Hofmann it is described that the polyamide layer and the low- and high-viscosity polyolefin layer are separated by a third layer, which is a mixture of

polypropylene and polyamide. Hofmann does not describe a multilayer film containing a polyamide layer and a polyolefin layer *directly connected to the polyamide layer or connected by an adhesive layer*. The inner layer as described by Hofmann cannot be considered an adhesive layer, which is defined in the present application on page 4, lines 24-31.

Hofmann is thus merely an example of a different solution to provide multilayer blown-films, with the drawback that mixtures have to be made or even an extra layer has to be incorporated. Nowhere in Hofmann are branched polyamides described, let alone that branched polyamides allow for higher processing rates and blow-up ratios in multilayer films which contain a branched polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected to the polyamide layer by an adhesive layer.

A person ordinarily skilled in the art would therefore not obtain the presently claimed invention from Joachimi et al and Hofmann since Hofmann does not describe a multi layer film, in which a polyamide layer and a polyolefin layer are directly connected to the polyamide layer or connected by an adhesive layer and Joachimi does not relate to processes for blown film and problems associated therewith.

Therefore reversal of the Examiner's rejection of claims 1, 5, 8, 18, 12-17, 22-25 under 35 USC 103(a) over Joachimi et al in view of Hofmann is in order.

2. Claims 1, 5, 9-11, 19-21, 26 and 28 are patentably unobvious under 35 USC 103(a) over Joachimi et al in view of Ramesh

The comments above are equally germane to the *unobviousness* of claims 1, 5, 9-11, 19-21, 26 and 28 are patentably unobvious under 35 USC 103(a) over Joachimi et al in view of Ramesh.

In this regard, Ramesh discloses a multilayer blown film with various layers. In column 17, lines 3-17, the problem addressed by Ramesh is that prolonged heating

results in bubble instability. A solution to this problem is also described, namely to heat by infrared in order to avoid prolonged heating. When this solution is applied "...one or more core polyolefin layers are *not* needed." (column 17, lines 14 and 15, emphasis added) Ramesh thus also points towards using extra layers of polyolefin in order to obtain good bubble stability or to use a different heating method. Ramesh also does not disclose branched polyamides.

A person wishing to obtain higher processing rates and blow-up ratios for a multilayer film containing a polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected by an adhesive layer would therefore not arrive at the presently claimed invention by consulting Ramesh, as Ramesh proposes a different, more complex solution. One would also not come to the presently claimed invention by combining Ramesh with Joachimi, as Joachimi does not relate to processes for blown film and problems associated therewith and Ramesh provides a different, more complex solution.

Therefore reversal of the rejection of claims 1, 5, 9-11, 19-21, 26 and 28 as obvious under 35 USC 103(a) over Joachimi et al in view of Ramesh is in order.

3. Claims 27 and 29 are patentably unobvious under 35 USC 103(a) over Joachimi et al in view of Ramesh and further in view of Dobreski et al

With respect to the rejection of claims 27 and 29 as allegedly obvious under 35 USC 103(a) over Joachimi et al in view of Ramesh and further in view of Dobreski et al, the applicants note that Dobreski et al merely describes a blown film made from a blend comprising LLDPE (linear low density ethylene copolymer) and poly(methyl methacrylate). Dobreski does not relate to multilayer film, let alone to multilayer films in which one layer is a polyamide. As elaborated in the originally filed specification and discussed briefly above, layers of LLDPE in films are known for their high tear strength. (Please see in this regard the present application at page 1, lines 9-12.)

A person wishing to obtain higher processing rates and blow-up ratios for a multilayer film containing a polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected by an adhesive layer, would therefore not come to the presently claimed invention by consulting Joachimi, Ramesh and Dobreski et al, as Dobreski et al does not relate to multilayer film, and teaches to use a blend for the LLDPE layer. Nowhere in Dobreski et al is polyamide layers mentioned. And, as discussed previously Joachimi does not relate to a process for preparing blown film and problems associated therewith, let alone that branched polyamide results in higher processing rates and blow-up ratio while Ramesh also teaches towards a different solution.

Therefore to combine Dobreski et al with Joachimi and Ramesh appears to be based on impermissible hindsight. None of the applied publications give a reasonable expectation for success and none make it obvious to try to use a branched polyamide in order to increase processing rates and blow-up ratios for a multilayer blown film containing a polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected by an adhesive layer.

Therefore, reversal of the rejection of claims 27 and 29 under 35 USC §103(a) based on the combination of Joachimi, Ramesh and Dobreski et al is likewise in order.

DE KROON et al
Serial No. 10/511,344
April 8, 2010

4. Conclusion.

For the reasons advanced, the Examiner's rejections of the pending claims herein under 35 USC §103(a) are in error and must be reversed. Such favorable action is solicited.

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: /Bryan H. Davidson/
Bryan H. Davidson
Reg. No. 30,251

BHD:dlb
1100 North Glebe Road, 8th Floor
Arlington, VA 22201-4714
Telephone: (703) 816-4000
Facsimile: (703) 816-4100

VIII. CLAIMS APPENDIX

1. (Previously Presented) Process for producing a multilayer film comprised of a polyamide layer and a polyolefin layer, the process comprising forming by blown-film processing a multilayer film containing at least a branched polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected to the polyamide layer by an adhesive layer, wherein said branched polyamide layer consists of a branched polyamide, and said polyolefin layer consists essentially of polypropylene or LLDPE containing at most 5% of another polyethylene.
- 2.-4. (Cancelled)
5. (Previously Presented) Multilayer film formed by blown-film processing comprising at least a polyamide layer and a polyolefin layer directly connected to the polyamide layer or connected to the polyamide layer by an adhesive layer, wherein the polyamide layer consists of a branched polyamide, and wherein the polyolefin layer consists essentially of polypropylene or of polyethylene, which polyethylene layer, other than the adhesive layer, if present, contain only polyethylene which is at least 95% linear low-density polyethylene.
- 6 - 7. (Cancelled)
8. (Previously Presented) Multilayer film according to claim 5, wherein the polyolefin layer consists essentially of linear polypropylene.
9. (Previously Presented) Multilayer film according to claim 5, wherein the polyolefin layer consists essentially of linear low density polyethylene.
10. (Previously Presented) Multilayer film according to claim 9, wherein the polyolefin layer includes essentially 0% of another polyethylene characterized by good bubble stability in a blow molding process.

11. (Previously Presented) Multilayer film according to claim 5, wherein the polyolefin layer consists of linear low density polyethylene alone or in mixture with up to 50% of modified linear low density polyethylene adhesion modifier, as the only polyolefin material(s).
12. (Previously Presented) Multilayer film according to claim 5, having a total thickness in the range of from 20 to 300 μm .
13. (Previously Presented) Multilayer film according to claim 5, wherein the polyolefin layer has a thickness of from 10 μm to about 100 μm .
14. (Previously Presented) Multilayer film according to claim 13, wherein the polyamide layer has a thickness of from 2 to 150 μm .
15. (Previously Presented) Multilayer film according to claim 13, wherein the polyamide film has a thickness of at least 20% of the thickness of the polyolefin layer up to 100 μm .
16. (Previously Presented) A blown film comprising the multilayer film according to claim 5.
17. (Previously Presented) Blown film according to claim 16, wherein the blown film has a blow-up ratio of from 20 to 40%.
18. (Previously Presented) Process according to claim 1, wherein the polyolefin layer consists essentially of linear polypropylene.
19. (Previously Presented) Process according to claim 1, wherein the polyolefin layer consists essentially of linear low density polyethylene.
20. (Previously Presented) Process according to claim 19, wherein the polyolefin layer includes essentially 0% of another polyethylene characterized by good bubble stability in a blow molding process.
21. (Previously Presented) Process according to claim 1, wherein the polyolefin layer consists of linear low density polyethylene alone or in mixture with up to 50% of

modified linear low density polyethylene adhesion modifier, as the only polyolefin material(s)

22. (Previously Presented) Process according to claim 1, wherein the blow-molded multilayer film has a total thickness in the range of from 20 to 300 μm .
23. (Previously Presented) Process according to claim 1, wherein the polyolefin layer of the blow-molded multilayer film has a thickness of from 10 μm to about 100 μm .
24. (Previously Presented) Process according to claim 23, wherein the polyamide layer has a thickness of from 2 to 150 μm .
25. (Previously Presented) Process according to claim 23, wherein the polyamide film has a thickness of at least 20% of the thickness of the polyolefin layer up to 100 μm .
26. (Previously Presented) Process for producing a multilayer film comprising forming by blown-film processing a multilayer film comprising outer polyolefin layers and an intermediate polyamide layer, wherein the outer polyolefin layers consist of a linear low density polyethylene (LLDPE), 0-10 wt.% of a polyethylene other than LLDPE, and optionally between 10 to 50 wt.% of a modified LLDPE as an adhesion modifier, and wherein the polyamide layer consists of a branched polyamide layer.
27. (Previously Presented) Process according to claim 26, wherein the outer layers consist of a mixture of 90 wt.% LLDPE and 10 wt.% of modified LLDPE as an adhesion promoter.
28. (Previously Presented) A multilayer blown-film comprising outer polyolefin layers and an intermediate polyamide layer, wherein the outer polyolefin layers consist of a linear low density polyethylene (LLDPE), 0-10 wt.% of a polyethylene other than LLDPE, and optionally between 10 to 50 wt.% of a modified LLDPE as an

adhesion modifier, and wherein the polyamide layer consists of a branched polyamide layer.

29. (Previously Presented) A multi-layer blown film according to claim 28, wherein the outer layers consist of a mixture of 90 wt.% LLDPE and 10 wt.% of modified LLDPE as an adhesion promoter.

IX. EVIDENCE APPENDIX

Appeal Brief Exhibit	<u>Evidence Title</u>	<u>Record Entry</u>⁴
1.	"Declaration Under Rule 132" of Ted BRINK	Submitted and entered into the record with "Response After Final Rejection" dated March 21, 2008
2.	"Supplemental Declaration Under Rule 132" of Jan DE KROON, Ted BRINK and Atze Jan NIJENHUIS	Submitted and entered into the record with "Amendment VI" dated July 27, 2009
3.	Kim et al, Polymer Engineering and Science, 2004, vol. 44, no. 2 pages 283-302	Submitted as Exhibit A to and entered into the record with "Amendment" dated December 29, 2008
4.	Kirk-Othmar Encyclopedia of Chemical Technology, "Film and Sheet Materials", 3.1.1 Blown Film	Submitted as Exhibit B to and entered into the record with "Amendment" dated December 29, 2008

⁴ The date of record entry noted herein is intended to be the statement of record entry required by 37 CFR § 141.37(c)(1)(ix).

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

DE KROON et al

Atty. Ref.: 4662-254

Serial No. 10/511,344

Group: 1711

Filed: May 23, 2005

Examiner: Haider

For: MULTILAYER BLOWN FILM AND PROCESS FO PRODUCTION THEREOF

* * * * *

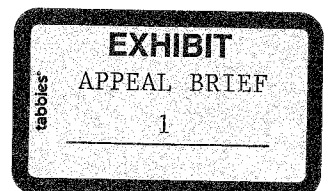
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER RULE 132

Sir:

Pursuant to 37 CFR §1.132, the undersigned, **Ted BRINK**, hereby declares and states that:

1. I am presently and for all times relevant to the facts stated herein have been employed by DSM N.V. at its facility in Geleen, The Netherlands.
2. I am a named inventor of, and am thereby familiar with, the invention disclosed and claimed in U.S. Patent Application Serial No. 10/511,344 filed on May 23, 2005, entitled "MULTILAYER BLOWN FILM AND PROCESS FOR PRODUCTION THEREOF" (hereinafter "the '344 application").
3. I am therefore familiar with the experimental evidence presented originally in the '344 application, particularly Examples I through III and Comparative Experiments A and B as reported on pages 6 and 7 of the '344 application. As to such experimental evidence, I offer the following



additional comments and observations based on my personal experiences when such experimental evidence was created:

Comparative Experiment A and Example I

The bubble stability in Example I where the polyamide (PA) layer is the branched polyamide-6 (PA6) has a better bubble stability than Comparative Experiment A where the inner layer is the standard linear (non-branched) PA6. The bubble stability was determined visually by observing the degree of vibrations of the film. My observations were that the blow moulded multilayer film of Example I clearly exhibited significantly higher bubble stability with a lower degree of vibration during blow-moulding as compared to Comparative Experiment A.

Comparative Experiment B

In this comparative experiment, the process of Comparative Experiment A was repeated, except that 30 wt.% LDPE in the outer layer of PE mixture was replaced with LLDPE so that the PE layer was formed of a mixture of 90 wt.% LLDPE and 10wt.% Yparex 0H040. It was clear from visual inspection that such a change had a strong influence on the bubble stability. Specifically, replacing 30wt% LDPE with LLDPE so that the PE layer had 90 wt% LLDPE (instead of 60wt% LLDPE) made it impossible to control the blow-moulding process in such a way as to obtain a bubble with sufficient stability. It was observed in this regard that strong bubble vibrations occurred when the multilayer film of Comparative Experiment B was blow-moulded resulting in frequent bubble collapse.

DE KROON et al
Serial No. 10/511,344

Example II and III

This experimental evidence was obtained under the same conditions as Comparative Experiment B, except the linear PA6 was replaced with the branched PA6 employed in Example I. When blow-moulded, the bubble remained stable. The good stability of the bubble was also confirmed by the fact that it was possible to increase the blow-up ratio from 2.1 to 2.5.

4. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,

March 15, 2008
Date Signed


Ted BRINK

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

DE KROON et al

Atty. Ref.: 4662-254

Serial No. 10/511,344

Group: 1711

Filed: May 23, 2005

Examiner: Haider

For: MULTILAYER BLOWN FILM AND PROCESS FO PRODUCTION THEREOF

* * * * *

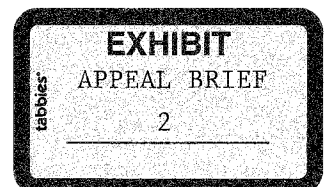
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

SUPPLEMENTAL DECLARATION UNDER RULE 132

Sir:

Pursuant to 37 CFR §1.132, the undersigned, Jan DE KROON, Ted BRINK, and Atze Jan NIJENHUIS hereby declare and state that:

1. We are named co-inventors of the invention disclosed and claimed in U.S. Patent Application Serial No. 10/511,344 filed on May 23, 2005, entitled "MULTILAYER BLOWN FILM AND PROCESS FOR PRODUCTION THEREOF" (hereinafter "the '344 application"), and for all times relevant to the facts stated herein have been employed by DSM N.V. at its facility in Geleen, The Netherlands.
2. It was just recently brought to our attention that certain terminology that was used to describe the invention in the '344 application was not entirely accurate and has therefore led to some confusion with respect to the subject matter being claimed therein.
3. Specifically, it was just brought to our attention that the term "blow-molding" was employed in the '344 application to describe the general



melt-processing technique of the present invention. The use of "blow-molding" to describe the invention of the '344 application was an unfortunate choice of terminology since it connotes that a mold (and hence a mold cavity) is employed to form a hollow structure. No such mold is in fact employed by the invention of the '344 application as it is related to a "blown-film process".

4. It has now been fully realized that a "blow-molding" technique is known in the art as one in which a molten tube of resin (called a "parison") is extruded from a circular die into an open mold. The mold is thereafter closed around the parison and air under pressure is fed through the die into the parison which expands the resin tube so as to fill the mold. The expanded tube is then allowed to cool inside the mold so that, upon opening of the mold, a hollow three-dimensional shaped part is obtained.¹
5. In a "blown film process", a tubular die is employed through which a tube of resin film is extruded in a tower having a collapsing frame at the top. The collapsing frame collapses the extruded film tube so that the tube diameter can be expanded by the introduction of air through the die. The expanded diameter film tube, termed a film "bubble" is cooled in a cooling zone between the extrusion die and the collapsing frame. The collapsed film is typically subjected to slitting and winding operations downstream of the collapsing frame.² A description of one conventional "blown film process" is found in US Patent No. 4,101,614, attached hereto as Exhibit 3.

¹ See in this regard, the attached Exhibit 1 from Kirk-Othmer Encyclopedia of Chemical Technology, 1981, vol. 0, pages 11-12 and 31.

² See in this regard, the attached Exhibit 2 from Kirk-Othmer Encyclopedia of Chemical Technology, 1981, vol. 0, pages 6 and 26.

6. That the intent of the '344 application to describe a "blown film process" is apparent in the Examples thereof. Specifically, at page 6, line 8 under "Comparative Experiment A and Example I", we note that:

"...a *Bandera blown film line* [was used] equipped with 3 extruders each having an annular die 100 mm in diameter [to form] a film bubble...."

7. Bandera systems are well known to form blown film as evidenced by the following articles:

http://www.luigibandera.it/pdf/1173716444_news_0307_ENG.pdf

<http://www.film.luigibandera.com/product/indexprod.asp>

8. As is evident from the discussion above, therefore, a mold with its attendant mold cavity is not employed in the practice of the invention of the '344 application. Instead, a blown-film process is employed wherein the resulting product is a multilayer film, not a hollow three-dimensional shaped part.
9. We now fully realize that the term "blow moulding" as used in the '344 application occurred by inadvertent error which was the result of our not fully comprehending art recognized meaning of such term. Instead, it was our intent to describe an invention wherein a film is produced by blowing up an extruded film tube, cooling the extruded film tube and then collapsing the same. That is, it is now realized that we should have more accurately used the term "blown film" to describe the process of the '344 application.

10. The inadvertent use of the inaccurate terminology as discussed above was most recently employed in the "Declaration Under Rule 132" which was executed by the undersigned, Ted Brink, and was filed in the '344 application with the "Response After Final Rejection" on March 21, 2008. At that time, the term "blow-molding" was in fact intended to refer to "blown film processing" for the reasons noted above. In order to ensure clarity in the record, the facts stated in such prior Declaration are restated below with the exception being that accurate terminology has been employed:

Comparative Experiment A and Example I

The bubble stability in Example I where the polyamide (PA) layer is the branched polyamide-6 (PA6) has a better bubble stability than Comparative Experiment A where the inner layer is the standard linear (non-branched) PA6. The bubble stability was determined visually by observing the degree of vibrations of the film. My observations were that the multilayer film of Example I clearly exhibited significantly higher bubble stability with a lower degree of vibration during blown film processing as compared to Comparative Experiment A.

Comparative Experiment B

In this comparative experiment, the process of Comparative Experiment A was repeated, except that 30 wt.% LDPE in the outer layer of PE mixture was replaced with LLDPE so that the PE layer was formed of a mixture of 90 wt.% LLDPE and 10wt.% Yparex 0H040. It was clear from visual inspection that

such a change had a strong influence on the bubble stability. Specifically, replacing 30wt% LDPE with LLDPE so that the PE layer had 90 wt% LLDPE (instead of 60wt% LLDPE) made it impossible to control the blown film process in such a way as to obtain a bubble with sufficient stability. It was observed in this regard that strong bubble vibrations occurred when the multilayer film of Comparative Experiment B was formed by blown film processing resulting in frequent bubble collapse.

Example II and III

This experimental evidence was obtained under the same conditions as Comparative Experiment B, except the linear PA6 was replaced with the branched PA6 employed in Example I. When formed by blown film processing, the bubble remained stable. The good stability of the bubble was also confirmed by the fact that it was possible to increase the blow-up ratio from 2.1 to 2.5.

11. We declare further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

DE KROON et al
Serial No. 10/511,344

Respectfully Submitted,

Date Signed

Jan DE KROON

Date Signed

Ted BRINK

24-06-2009

Date Signed

[Signature]

Atze Jan NIJENHUIS

(41,59,60). It is most frequently used with polyethylene, high impact polystyrene, polypropylene, and several engineering resins. Some modifications to the resin, machine, and mold are required, and a blowing agent must be added to the resin. A chemical blowing agent, which releases gas when heated, is commonly used. The choice of blowing agents depends on the processing temperature required. The most common blowing agent is azodicarbonamide (1,1'-azobisformamide) used at 200–260°C. Upon decomposition, it releases nitrogen, carbon monoxide, and carbon dioxide (qv). Approximately 0.5 wt % of a blowing agent is normally added to the resin pellet as a surface coating or as a pelletized concentrate. Instead of a chemical blowing agent, nitrogen may be mixed with the melt while it is under pressure in an extruder and the mixture maintained under pressure until it is injected into the mold.

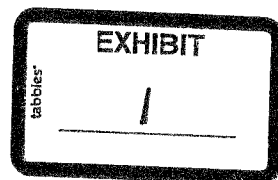
The injection molding machine must be equipped with a shutoff nozzle that maintains the melt under pressure while the mold is opened. The screw is retracted only part of the way needed for a full shot, and a short shot is injected into the mold. Without a blowing agent, only a section of a part, ie, a short shot, would be made; the empty space allows the blowing agent to expand the melt, forming the foam structure. Structural foam molding is limited to parts with wall thicknesses of at least 6 mm; below that thickness, reduction in part weight is usually insignificant. Parts, typically, have a dense skin and a foamed interior with various pore sizes. Compared to injection molded surfaces, the surfaces of structural-foam moldings are poor, and are characterized by a rough, swirly finish. Maximum pressure in the mold during foaming is much lower than in injection molding; also, no packing pressure needs to be maintained since the gas keeps the melt front moving. Surface appearance is improved by special techniques.

Because of low injection pressure, some cost savings are possible in mold and press construction. Molding cycles are somewhat longer than for injection molding. The part must be cooled in the mold long enough to be able to resist swelling from internal gas pressure. In structural foam parts there is almost a total absence of sink marks, even in the case of unequal section thickness. Structural foam has replaced wood, concrete, solid plastics, and metals in a variety of applications.

Blow Molding. Blow molding is the most common process for making hollow thermoplastic components (61–63). In extrusion blow molding a molten tube of resin called a parison is extruded from a die into an open mold (Fig. 15a). In Figure 15b the mold is closed around the parison, and the bottom of the parison is pinched together by the mold. Air under pressure is fed through the die into the parison, which expands to fill the mold. The part is cooled as it is held under internal air pressure. Figure 15c shows the open mold with the part falling free.

As the parison is extruded, the melt is free to swell and sag. The process requires a viscous resin with consistent swell and sag melt properties. For a large container the machine is usually equipped with a cylinder and a piston called an accumulator. The accumulator is filled with melt from the extruder and emptied at a much faster rate to form a large parison; this minimizes the sag of the molten tube.

With a simple parison, the large-diameter sections of the bottle have a thin wall and the small-diameter sections have a thick wall. Certain modifications of



the die can control the thickness of the parison wall along its length, which results in a bottle with improved wall thickness distribution and better strength. The most common blow molding resin is HDPE used to produce containers ranging in size from 30 cm³ to 200 L.

In injection blow molding, a parison is injection molded onto a core pin; the parison is then rapidly transferred via the core pin to a blow mold, where it is blown by air into an article. This process is applied to small and intricate bottles.

Soft-drink bottles made from PET are usually made by stretch-blow molding in a two-step process. First, a test-tube-shaped preform is molded, which is then reheated to just above its glass-transition temperature, stretched, and blown. Stretching the PET produces biaxial orientation, which improves transparency, strength, and toughness of the bottle. A one-step process is used for many custom containers that are injection stretch-blow molded.

Development—trends in blow molding focus on the optimization of the viscoelastic properties and improvement in thermal stability of polymers other than HDPE to develop new extrusion–injection blow molding grades; fabrication of small containers by multilayer blow molding for improved barrier properties to water, oxygen or hydrocarbons; prediction through software packages of wall thickness for parisons and final parts to minimize materials usage.

4.2. Rotational Molding. Hollow articles and large, complex shapes are made by rotational molding, usually from polyethylene powder of relatively low viscosity (64–66). The resin is in the form of a fine powder. A measured quantity is placed inside an aluminum mold and the mold is heated in an oven and rotated at low speed. The resin sinters and fuses, coating the inside of the mold. The mold is then cooled by water spray and the part solidifies, duplicating the inside of the mold.

A rotomolding machine has three long arms extending from a central driving mechanism; each arm rotates several molds in two planes. The arms are moved from one process station to the next, ie, from unloading and loading to heating and cooling. Tooling costs are low. The molds are usually made of cast aluminum, but sheet metal is also used. The melt is forced without pressure against the mold surface during heating or cooling, resulting in uniform wall thickness, zero orientation, and high physical properties. Cycle times are long because of the heating and cooling required; they depend on wall thickness and can be as high as 15 min for a 4-mm wall thickness. Common rotomolded products include large tanks and boxes, drums, furniture, and toys. The PVC plastisol, a mixture of fine PVC particles and a plasticizer, may also be processed by rotomolding. Plastisols are liquid at room temperature and are converted to soft solids when heated to ca 180°C. Playballs and toys are made from plastisols.

Among recent trends and developments in rotomolding are the use of microprocessors and temperature sensors for quality assurance, the refinement of methods to produce multiwalled solid or foamed structures all coupled with the continuing availability of new resin grades with suitable viscosities and high thermo oxidative stability over the prolonged periods of time in the oven.

4.3. Expandable Polystyrene Molding. Molding expandable polystyrene gives foamed products such as insulation board shapes for packaging and disposable food and cup containers. Such processes are also called bead or steam molding (67,68). Expandable polystyrene moldings are manufactured

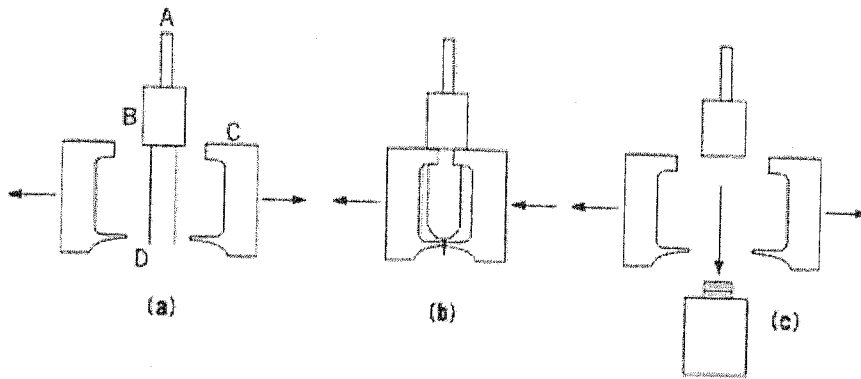


Fig. 15. Three stages of blow molding (a-c): A, air line; B, die; C, mold; and D, parison. See text.

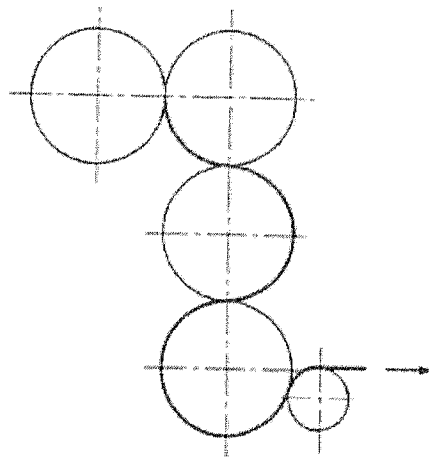


Fig. 16. A four-roll, inverted "L" calender.

3.5. Blown Film. The blown film process (Fig. 6) uses a tubular die from which the extrudate expands in diameter while traveling upward to a film tower. The top of the tower has a collapsing frame followed by guide and pull rolls to transport the collapsed film to subsequent slitting and windup rolls. The tubular bubble from the die is inflated to the desired diameter by air passing through the center of the die. Although primary cooling to solidify the melt is supplied by an external air ring, chilled air may also be used internally. Polyethylene is the primary plastic used in most films, especially for packaging and trash bags. Coaxial dies can be used for manufacture of coextruded multilayer films.

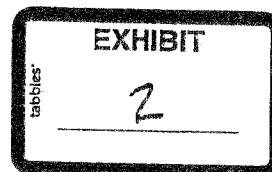
The tube is characterized by its blow-up ratio, ie, a larger diameter than the die opening, which is expressed as the ratio of bubble diameter to the die diameter. Typical blow-up ratios range from 2:1 to 4:1. The final film thickness is much thinner than the die gap. Die gaps are slits of ~ 0.65 mm. Typical film thicknesses are 0.007–0.125 mm. The process requires a high melt viscosity resin so that the melt can be pulled from the die in an upward direction. Since only air is used for cooling, removal of heat tends to be slow and rate limiting. Chilled air can also be used internally to improve the efficiency of the air cooling process. The film may be treated for subsequent printing, and it can be slit into various widths and wound onto separate cores.

3.6. Cast Film. The cast film process provides a film with gloss and sparkle and can be used with various resins. Figure 7 is an illustration of the essential features of the extrusion equipment. The die opening is a long straight slit with an adjustable gap ~ 0.4 mm wide. The die is positioned carefully with respect to the casting roll. The casting or chill roll is highly polished and plated and imparts a smooth and virtually flawless surface to the film. The roll is cooled by rapid circulation of water. Temperature control is critical. A die somewhat longer than the width of the film is needed, because the molten web becomes narrow as it is drawn from the die; this is called neck-in. Edges of the film thicken and are mechanically removed before the film is wound on a roll. The edge trim can be reprocessed.

One of the requirements of this process is that the melt maintain good contact with the chill roll, ie, air must not pass between the film and the roll. Otherwise, air insulates the plastic and causes it to cool at a rate different from the rest of the plastic and this spoils the appearance of an otherwise satisfactory product. The melt should not emit volatiles, which condense on the chill roll, reduce heat transfer, and mar the film's appearance. The cast film process allows the use of a higher melt temperature than is characteristic of the blown film process. The higher temperature imparts better optical properties.

Film stretching is a process to impart biaxial orientation in the film by stretching it in two directions simultaneously, the transverse and machine directions, respectively. The process is carried out in a device that grips the edges of the film and extends them to larger widths as the film moves from the inlet to the exit roller. The objective is to increase the modulus and strength of the film uniformly along the entire film plane. Both PP and PET have been used successfully in this process (37).

3.7. Sheet. The process used to make an extruded plastic sheet is illustrated in Figure 8. Sheet thicknesses are 0.25–5 mm and widths are as great as 3 m. Heavier gauge sheets are usually cut to a specified length and



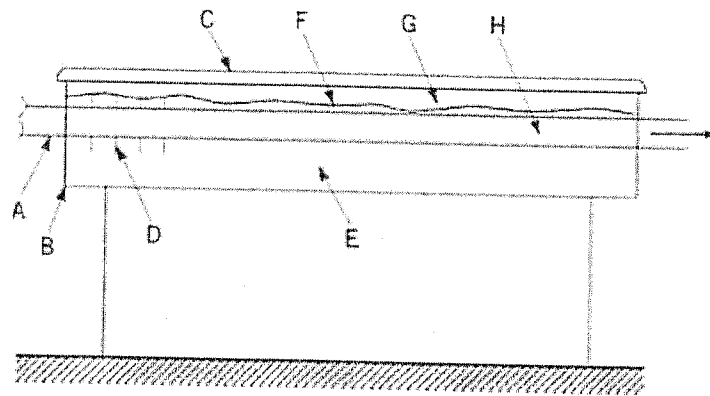


Fig. 5. Vacuum calibrator for pipe and tubing extrusion: A, molten tube from die; B, tank; C, hinged cover with gasket; D, sizing rings; E, circulated and temperature controlled water; F, water level; G, vacuum; and H, inside of pipe open to atmospheric pressure (20).

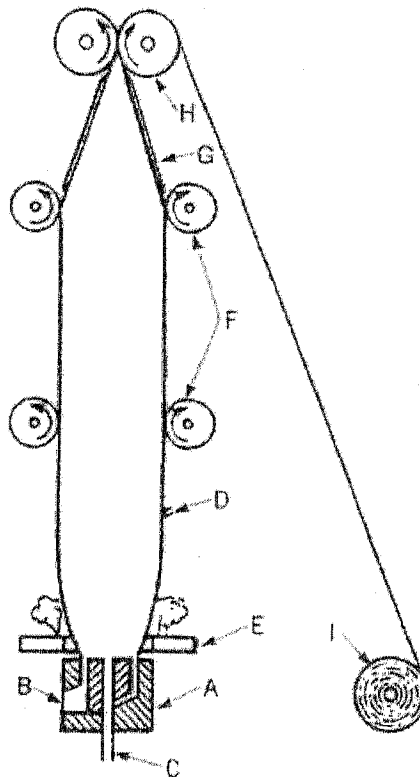


Fig. 6. Extrusion of blown film: A, blown-film die; B, die inlet; C, air hole and valve; D, plastic tube (bubble); E, air ring for cooling; F, guide rolls; G, collapsing frame; H, pull rolls; and I, windup roll (20).

[54] **BLOWN FILM PROCESS**

[75] Inventor: Carl B. Havens, Fresno, Calif.

[73] Assignee: The Dow Chemical Company,
Midland, Mich.

[21] Appl. No.: 710,984

[22] Filed: Aug. 2, 1976

Related U.S. Application Data

[63] Continuation of Ser. No. 554,951, Mar. 3, 1975,
abandoned, which is a continuation of Ser. No.
376,834, Jul. 5, 1973, abandoned.

[51] Int. Cl.² B29F 3/08
[52] U.S. Cl. 264/40.6; 264/95;
264/237; 425/143; 425/326.1
[58] Field of Search 264/89, 95, 210 R, 237,
264/40.1, 348, 40.6; 425/143, 170, 72, 326 R,
326.1

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,092,874 6/1963 Fallwell 264/40.1
3,125,616 3/1964 Cook et al. 264/40.1

OTHER PUBLICATIONS

Film Cooling & Frost Line-Polyethylene Film Extrusion-An Operating Manual - U.S.I.-1960-Nat. Dist. & Chem. Corp. pp. 27-30.

"Effect of Extrusion Variables on the Fundamental Properties of Tubular Film"-Plastics, 4-1961 -vol. 26 -Clegg - pp. 114-116.

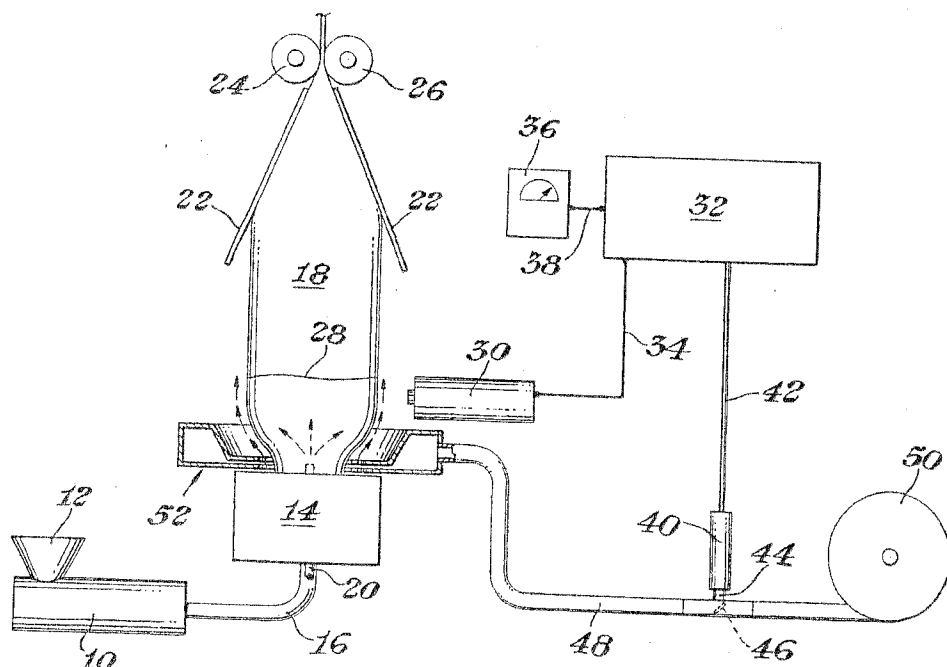
Primary Examiner-Jeffery R. Thurlow
Attorney, Agent, or Firm-Burke M. Halldorson;
Tai-Sam Choo

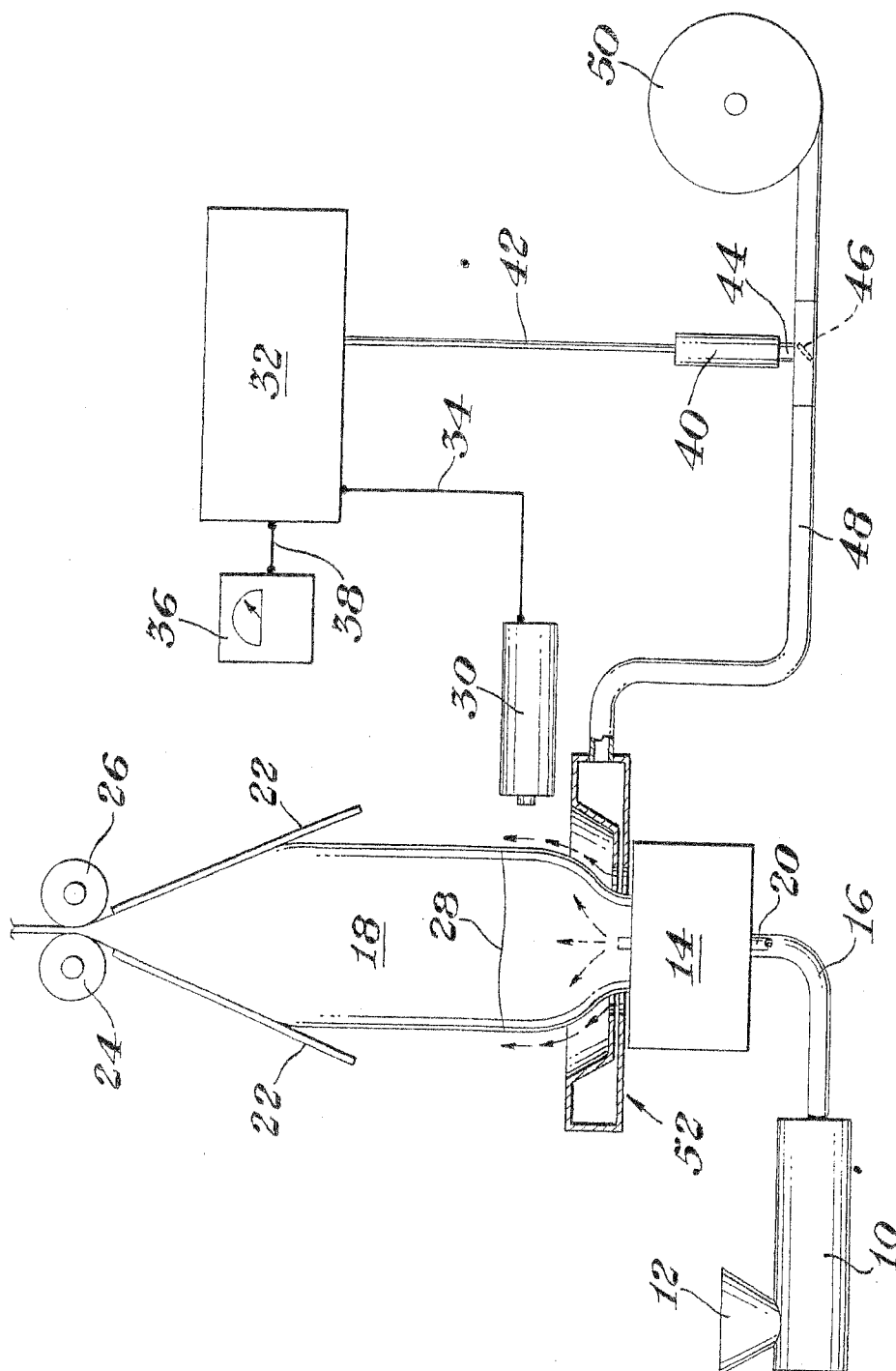
[57]

ABSTRACT

A blown film process wherein: the temperature of the film is continually monitored in a select control or target area that is remote from the film frost line; a control of "target temperature" is determined based empirically or otherwise on a given set of companion operating conditions; and a variable film cooling source or supply is regulated to establish the control temperature as an essentially constant or non-variable operating condition. The process is characterized by an essentially stable frost line position and to the extent movement of the frost line can be optically or otherwise observed or sensed, and an appropriate signal derived therefrom, the process can be alternately practiced based on monitoring the position of the frost line, defining a control or "target" frost line position, and regulating a film cooling source responsive to deviances or movement from the control position.

2 Claims, 1 Drawing Figure





BLOWN FILM PROCESS

This application is a continuation of prior application Ser. No. 554,951, filed Mar. 3, 1975, now abandoned, and which is a continuation of application Ser. No. 376,834, filed July 5, 1973, now abandoned.

FIELD OF THE INVENTION

The blown film process as expressed or intended herein, is meant to refer broadly to the manufacture of plastic film (including sheet materials) through extruding a continuous molten tube of heat plastified resin, stretching or drawing the tube about a trapped air or gas bubble, and simultaneously cooling the plastic such as by external or internal cooling means. The invention particularly relates to such a process wherein a control area is defined, a control temperature determined for such area, and maintained through variable cooling steps, whereby improved film quality, and/or increased maximum production rates or ceilings are achieved. Alternately the invention concerns defining a controlled frost line position, monitoring such position, and providing a variable cooling means to correct deviations therefrom, for essentially like purposes and improved results.

BACKGROUND OF THE INVENTION

The ultimate properties and quality of blown film can be adversely affected particularly by cyclic variations in operating conditions, and by less than perfect regularity and consistency as regards the extruded resin. For example the temperature of the extrusion apparatus tends to have inherent cyclic character. Also cyclic conditions occur in conventional film cooling systems, whether based on a refrigerated source or if taken from ambient air. Additionally, film extruders frequently require a filtering system that will gradually clog with impurities, thus inducing a variable effect, particularly a change in melt index, in the resin passed through the filter. The resin itself may not be entirely consistent in quality, such as its melt index value and melt temperature.

Operating inconsistencies such of the above type can produce poor film in the sense of poor film flatness (i.e. appearance of wrinkles in the film) and poor uniformity of the gauge profile of the film. The gauge profile can be somewhat controlled by thickness measuring devices and systems, which give the operator some indication and warning when profile control is deteriorating, so that the appropriate control corrections can be made. However, when conditions go awry causing wrinkles to appear, there have not been good devices to predict this approaching condition, and to give the operator adequate warning to make appropriate corrections.

Thus even with close attention by a skilled operator, it has been difficult to control film quality above certain ceiling production rates. Even when operating within a production range considered manageable by a skilled operator, the film quality can be less than desired and less than specification tolerances, due to imprecise and inadequate control over cyclic and/or fluctuating operating conditions.

Accordingly, it would be advantageous to the art if there were available a blown film process which achieved finer and more precise control over film quality and/or properties.

It would be particularly advantageous if such a process provided a sufficient automatic counter-balancing

effect to fluctuating and/or cyclic operating conditions to permit a significant increase in the possible rate of extrusion, while retaining an acceptable level of quality in the film produced, and/or which would consistently produce better quality film.

SUMMARY OF THE INVENTION

Briefly these and other objectives of the invention are achieved in blown film process using as a base control, the monitoring of a select control area of the film, or alternately, the monitoring of the position of the film frost line. A control temperature or control frost line position is determined which reflects the condition whereby good and preferably optimum quality film is produced, as per any given set of companion operating conditions. A variable cooling source is regulated responsive to signals received from the monitoring device, to stabilize and maintain the control temperature or control position, as applies, as an essentially constant operating condition. This system control provides precise, automatic control over film properties. It is particularly advantageous in providing prompt corrective response to the approaching condition of loss of film flatness, for which there has been inadequate warning or predicting systems in the past.

DETAILED DESCRIPTION OF THE INVENTION

The accompanying drawing illustrates a blown film process wherein there is represented and practiced a preferred embodiment of the inventive teaching and principles hereof.

Referring particularly to the drawing, a film forming resin is introduced into a heated extruder 10 through a hopper entry means 12, from whence it is eventually expelled in a heat plastified condition to a die head 14 by way of a connecting pipe or conduit 16. The resin emerges from the die in the form of a continuous tube or tubular envelope 18. The tube is stretched or drawn about a trapped bubble that is maintained and replenished by a regulated pressure line 20 that introduces generally controlled amounts of air or gas internally to the tube. A collapsing rack 22, and cooperating nip rolls 24 and 26, eventually collapse and flatten the tube at an area remote from the die head. This process will also typically include drive rolls comprising or located beyond nip rolls 24 and 26, to provide a pulling force to advance the tubing from the die. The speed of the drive rolls is controlled to stretch or draw the tubing longitudinally, and this speed factor, together with other controlling factors, will determine the circumferential size of this tube (i.e., whether it is distended, drawn-down, or maintained essentially the same as extruded size). The area of stretching occurs essentially between the die head and the film frost line shown at 28. Above the frost line, the film has advanced to a solidified or semi-solidified condition.

The invention particularly concerns a temperature sensing device 30 that is focused to read and continually monitor the temperature of the film in a control or target area that is underneath frost line 28, and above die head 14. The area of the film directly adjacent the frost line is not a good predictive or control area. This is presumably because of film crystallization effects near the frost line which tend to cause a stable temperature reading, or a reading which is not adequately predictive of changing conditions for which the control process hereof is designed to correct automatically. A good

predictive control area, however, will exist at an area remote from and spaced sufficiently downwardly from the frost line so as to be less influenced (or non-influenced) by crystallization effects occurring at and in the near vicinity of the frost line.

The signal produced by the temperature sensing device, or the output of this device, is fed to a controller or controlling means 32 through an electrical lead or connection 34, and also to a temperature reading or recording instrument 36, through an electrical lead or connection 38. The temperature reading instrument converts the signal to a dial reading, thus permitting the temperature in the control area to be determined numerically at any given time in the operation.

The output of the controller, is suited to operate an air motor or valve positioner device 40, through a pneumatic line connection 42 therewith. The valve positioner is connected by a suitable linkage assembly 44 to operate and position a butterfly type valve 46. The butterfly valve is inset in a cooling air or gas line 48 which delivers air from a blower or compressor unit 50, to a cooling ring 52 that is disposed about the lower extreme or tube 18, just above die head 14.

The system depends on the selection or determination of a control or target temperature for the control area. This is most expediently determined empirically, by arriving at a given set of operating conditions that produce optimum quality film. Upon determining a set of such conditions, the temperature in the control area is read and established as the control temperature. The dial reading while not essential in running the controls, permits the operator to observe and record, if desired, the temperature in the control area. The controller is set to continually compare the signal received from the sensing device, with the control temperature, or equivalently a pre-determined control signal. If the signal would indicate the temperature in the monitored area is rising, the controller notes the difference, and directs the valve positioner 40 to proportionately move the butterfly valve to permit increased air flow to cooling ring 52, to bring the temperature in the control area downwardly to the control temperature. Alternately a temperature drop is responded to by regulating the butterfly valve to decrease the flow or output of cooling ring 52. Necessarily the null position, that is, the position the valve assumes when reading a stable temperature condition, is at a point between the extreme open and extreme closed positions of the butterfly valve.

The invention may also be practiced utilizing the height or position of the frost line as the control indicator. The monitoring device would be modified to optically or otherwise read the frost line height and produce signals indicating deviances therefrom. The control frost line position can be determined as before, that is, by operating empirically to define a given set of conditions under which quality film is produced, and defining the control position as that at which the frost line resides under such conditions. The signal provided by the monitoring device would be fed to the controller, and compared with a control signal, and corrective action taken, as required, to regulate air line 48, to thereby maintain or stabilize the control position.

The control process taught herein is applicable broadly to the production of plastic film, from film forming synthetic resin materials, based on the blown film process(s). Representative examples of films typically produced by this process are: polyethylene and known copolymers of ethylene and various other copo-

lymerizing agents such as propylene, acrylic acid, ethyl acrylate, etc.; polypropylene and known copolymers thereof, film forming polyesters, polystyrene and known copolymers thereof, vinyls such as polyvinyl chloride; saran; film forming polyamides and the like.

The monitoring devices applicable for use in the invention would be heat sensing devices such as a suitable optical pyrometer or radiation thermometer, and thermal-couples or thermistors such as of the feather sensor type, applicable for delicate web materials. When the control is based on a controlled frost line position, a haze meter can be employed to read the position of the frost line, and to produce or generate a signal upon which to base or regulate the film cooling source.

The controller is preferably of the type adapted to compare the input signal from the monitoring device with a control signal, and provide an output signal that is generally proportional with the deviance, if any, of the input signal from the control signal.

The positioning device can be electrically or pneumatically driven, depending on the input signal, space available for same, valve type, and so forth. The butterfly valve shown may be replaced by numerous other regulating valve types, or other devices adapted to regulate the flow (or conceivably temperature) of the cooling gas or air supplied to the cooling ring. The blower can supply refrigerated or ambient gas or air as would be found most optimum or necessary for any given blown film process and resins. The cooling ring is necessarily in an area where it can influence the temperature of the film in the monitored area, or the height of the frost line, as applies. Most preferably the air ring is positioned generally in the area shown by the drawing. Understandably, other cooling devices can be substituted for the cooling ring shown, or employed together therewith (i.e., of the various types known to the art, such as internally positioned cooling devices).

Certain of the known blown film processes include operating modes that may necessitate some modification hereof in order to apply these teachings to such a process. For example, a revolving die head, or a revolving take-up assembly, or the like (i.e., such as to continually revolve tube 18), is oftentimes employed in the blown film process for certain resins and to produce certain end products. The process described above can and has been applied to a revolving blown film process, in a like control procedure as that described above, essentially without modification. However, under certain conditions, it may be desirable to read or monitor several control areas about a revolving tube, and/or to employ an integrator to average the temperature in the monitored area(s), and/or to regulate a cooling change only at specific intervals, such as after each complete revolution of the film, as may be found desirable or advantageous in any specific film line.

In addition to controlling the film properties or qualities explicitly mentioned above, the control temperature and/or control frost line position can also be determined to beneficially affect the more consistent attainment of film qualities such as relates to the properties of tear and impact strength, and film shrinkage characteristics. The control temperature or control frost line height, as applies, would thus be determined in regard to such properties, empirically or otherwise, to attain more consistent achievement thereof.

EXAMPLE I

The invention as described is applied to a polyethylene "revolving tube type" blown film process having a 20 inch diameter die head. An "IRCON MODLINE", non-contacting optical pyrometer or radiation thermometer, "Instrument Series 3400," is used as the instrument to sense and monitor the temperature of the film. A control area is defined that is at least about 3 inches below the frost line, and most optimally is about 9 inches below the frost line and at least about 6 inches above the die head. A control temperature of about 240° F is established. An "IRCON" proportional controller is employed, Instrument Series 3400, that receives continually the electrical output of the optical pyrometer and converts the same proportionally into a pneumatic output that controls an air piston motor having an integral butterfly valve. The latter unit or assembly is available under the trade designation "Valteck Vector One Butterfly Valve." An approximately 1500 CFM capacity blower unit is employed, and is operated at full capacity, subject to regulation only by the controlled position of the butterfly valve. The following Table I summarizes the results comparatively between control and no control situations, wherein: "Maximum Rate" refers to the maximum achievable rate possible, but not practical for commercial runs; and "Maximum Good Production" is the maximum rate at which "good" film is produced based on the qualities of acceptable film flatness and uniformity of gauge profile. The latter figures are given in lbs./hour and also 1000 lbs./month. The monthly figure reflects "down time" and other interruptions in the process.

TABLE I

Description	No Control	Control
Max. Rate- Lbs./Hr.	675	675
Max. Good Prod.- Lbs./Hr.	550	650
Max. Good Prod.- M Lbs./Mo.	380	419

EXAMPLE II

The control process hereof is also tested in a still higher volume, polyethylene blown process or produc-

tion line, employing 30 inch diameter die, the process being also of the revolving tube type. The control process and the apparatus for accomplishing the same, is essentially the same as described supra. The control temperature and control area is near the same as with Example I. Significantly increased production capacity, as compared with the "no control situation", is also demonstrated in this test, with the results being tabulated below.

TABLE II

Description	No Control	Control
Max. Rate- Lbs./Hr.	1000	1000
Max. Good Prod.- Lbs./Hr.	800	950
Max. Good Prod.- M Lbs./Mo.	439	520

What is claimed is:

1. In a blown film process wherein film is produced through extruding a continuous molten tube of a film forming heat plastified synthetic resinous material, stretching or drawing the tube about a trapped air or gas bubble, and simultaneously cooling the tube, the steps comprising: monitoring the temperature of the film in a controlled area that is positioned between the frost line and extrusion die head, the control area being remote from and spaced sufficiently downwardly from the frost line so as to be less influenced by crystallization effects, cooling the film about its circumference between the control area and extrusion die head, setting a control temperature for the control area, comparing the monitored temperature with the control temperature, increasing or decreasing the rate of said cooling step responsive to the conditions of upward or downward drift, respectively, of the monitored temperature from the control temperature, whereby the process is characterized by an essentially constant temperature in the control area irrespective of cyclic variations in the operating parameters of the process.

2. The process of claim 1 wherein said cooling step comprises the step of varying the rate of gas flow in an air ring positioned between the control area and extrusion die head.

* * * * *

50

55

60

65

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

DE KROON et al

Atty. Ref.: **4662-254**

Serial No. **10/511,344**

Group: **1711**

Filed: **May 23, 2005**

Examiner: **Haider**

For: **MULTILAYER BLOWN FILM AND PROCESS FO PRODUCTION THEREOF**

* * * * *

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

SUPPLEMENTAL DECLARATION UNDER RULE 132

Sir:

Pursuant to 37 CFR §1.132, the undersigned, **Jan DE KROON**, **Ted BRINK**, and **Atze Jan NIJENHUIS** hereby declare and state that:

1. We are named co-inventors of the invention disclosed and claimed in U.S. Patent Application Serial No. 10/511,344 filed on May 23, 2005, entitled "MULTILAYER BLOWN FILM AND PROCESS FOR PRODUCTION THEREOF" (hereinafter "the '344 application"), and for all times relevant to the facts stated herein have been employed by DSM N.V. at its facility in Geleen, The Netherlands.
2. It was just recently brought to our attention that certain terminology that was used to describe the invention in the '344 application was not entirely accurate and has therefore led to some confusion with respect to the subject matter being claimed therein.
3. Specifically, it was just brought to our attention that the term "blow-molding" was employed in the '344 application to describe the general

melt-processing technique of the present invention. The use of "blow-molding" to describe the invention of the '344 application was an unfortunate choice of terminology since it connotes that a mold (and hence a mold cavity) is employed to form a hollow structure. No such mold is in fact employed by the invention of the '344 application as it is related to a "blown-film process".

4. It has now been fully realized that a "blow-molding" technique is known in the art as one in which a molten tube of resin (called a "parison") is extruded from a circular die into an open mold. The mold is thereafter closed around the parison and air under pressure is fed through the die into the parison which expands the resin tube so as to fill the mold. The expanded tube is then allowed to cool inside the mold so that, upon opening of the mold, a hollow three-dimensional shaped part is obtained.¹
5. In a "blown film process", a tubular die is employed through which a tube of resin film is extruded in a tower having a collapsing frame at the top. The collapsing frame collapses the extruded film tube so that the tube diameter can be expanded by the introduction of air through the die. The expanded diameter film tube, termed a film "bubble" is cooled in a cooling zone between the extrusion die and the collapsing frame. The collapsed film is typically subjected to slitting and winding operations downstream of the collapsing frame.² A description of one conventional "blown film process" is found in US Patent No. 4,101,614, attached hereto as Exhibit 3.

¹ See in this regard, the attached Exhibit 1 from Kirk-Othmer Encyclopedia of Chemical Technology, 1981, vol. 0, pages 11-12 and 31.

² See in this regard, the attached Exhibit 2 from Kirk-Othmer Encyclopedia of Chemical Technology, 1981, vol. 0, pages 6 and 26.

6. That the intent of the '344 application to describe a "blown film process" is apparent in the Examples thereof. Specifically, at page 6, line 8 under "Comparative Experiment A and Example I", we note that:

"...a *Bandera blown film line* [was used] equipped with 3 extruders each having an annular die 100 mm in diameter [to form] a film bubble...."

7. Bandera systems are well known to form blown film as evidenced by the following articles:

http://www.luigibandera.it/pdf/1173716444_news_0307_ENG.pdf

<http://www.film.luigibandera.com/product/indexprod.asp>

8. As is evident from the discussion above, therefore, a mold with its attendant mold cavity is not employed in the practice of the invention of the '344 application. Instead, a blown-film process is employed wherein the resulting product is a multilayer film, not a hollow three-dimensional shaped part.
9. We now fully realize that the term "blow moulding" as used in the '344 application occurred by inadvertent error which was the result of our not fully comprehending art recognized meaning of such term. Instead, it was our intent to describe an invention wherein a film is produced by blowing up an extruded film tube, cooling the extruded film tube and then collapsing the same. That is, it is now realized that we should have more accurately used the term "blown film" to describe the process of the '344 application.

10. The inadvertent use of the inaccurate terminology as discussed above was most recently employed in the "Declaration Under Rule 132" which was executed by the undersigned, Ted Brink, and was filed in the '344 application with the "Response After Final Rejection" on March 21, 2008. At that time, the term "blow-molding" was in fact intended to refer to "blown film processing" for the reasons noted above. In order to ensure clarity in the record, the facts stated in such prior Declaration are restated below with the exception being that accurate terminology has been employed:

Comparative Experiment A and Example I

The bubble stability in Example I where the polyamide (PA) layer is the branched polyamide-6 (PA6) has a better bubble stability than Comparative Experiment A where the inner layer is the standard linear (non-branched) PA6. The bubble stability was determined visually by observing the degree of vibrations of the film. My observations were that the multilayer film of Example I clearly exhibited significantly higher bubble stability with a lower degree of vibration during blown film processing as compared to Comparative Experiment A.

Comparative Experiment B

In this comparative experiment, the process of Comparative Experiment A was repeated, except that 30 wt.% LDPE in the outer layer of PE mixture was replaced with LLDPE so that the PE layer was formed of a mixture of 90 wt.% LLDPE and 10wt.% Yparex 0H040. It was clear from visual inspection that

such a change had a strong influence on the bubble stability. Specifically, replacing 30wt% LDPE with LLDPE so that the PE layer had 90 wt% LLDPE (instead of 60wt% LLDPE) made it impossible to control the blown film process in such a way as to obtain a bubble with sufficient stability. It was observed in this regard that strong bubble vibrations occurred when the multilayer film of Comparative Experiment B was formed by blown film processing resulting in frequent bubble collapse.

Example II and III

This experimental evidence was obtained under the same conditions as Comparative Experiment B, except the linear PA6 was replaced with the branched PA6 employed in Example I. When formed by blown film processing, the bubble remained stable. The good stability of the bubble was also confirmed by the fact that it was possible to increase the blow-up ratio from 2.1 to 2.5.

11. We declare further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

DE KROON et al
Serial No. 10/511,344

Respectfully Submitted,

23/6-2009


Date Signed



Jan DE KROON

23/6/2009

Date Signed



Ted BRINK

Date Signed

Atze Jan NIJENHUIS

(41,59,60). It is most frequently used with polyethylene, high impact polystyrene, polypropylene, and several engineering resins. Some modifications to the resin, machine, and mold are required, and a blowing agent must be added to the resin. A chemical blowing agent, which releases gas when heated, is commonly used. The choice of blowing agents depends on the processing temperature required. The most common blowing agent is azodicarbonamide (1,1'-azobisformamide) used at 200–260°C. Upon decomposition, it releases nitrogen, carbon monoxide, and carbon dioxide (qv). Approximately 0.5 wt % of a blowing agent is normally added to the resin pellet as a surface coating or as a pelletized concentrate. Instead of a chemical blowing agent, nitrogen may be mixed with the melt while it is under pressure in an extruder and the mixture maintained under pressure until it is injected into the mold.

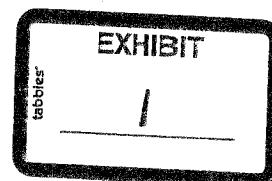
The injection molding machine must be equipped with a shutoff nozzle that maintains the melt under pressure while the mold is opened. The screw is retracted only part of the way needed for a full shot, and a short shot is injected into the mold. Without a blowing agent, only a section of a part, ie, a short shot, would be made; the empty space allows the blowing agent to expand the melt, forming the foam structure. Structural foam molding is limited to parts with wall thicknesses of at least 6 mm; below that thickness, reduction in part weight is usually insignificant. Parts, typically, have a dense skin and a foamed interior with various pore sizes. Compared to injection molded surfaces, the surfaces of structural-foam moldings are poor, and are characterized by a rough, swirly finish. Maximum pressure in the mold during foaming is much lower than in injection molding; also, no packing pressure needs to be maintained since the gas keeps the melt front moving. Surface appearance is improved by special techniques.

Because of low injection pressure, some cost savings are possible in mold and press construction. Molding cycles are somewhat longer than for injection molding. The part must be cooled in the mold long enough to be able to resist swelling from internal gas pressure. In structural foam parts there is almost a total absence of sink marks, even in the case of unequal section thickness. Structural foam has replaced wood, concrete, solid plastics, and metals in a variety of applications.

Blow Molding. Blow molding is the most common process for making hollow thermoplastic components (61–63). In extrusion blow molding a molten tube of resin called a parison is extruded from a die into an open mold (Fig. 15a). In Figure 15b the mold is closed around the parison, and the bottom of the parison is pinched together by the mold. Air under pressure is fed through the die into the parison, which expands to fill the mold. The part is cooled as it is held under internal air pressure. Figure 15c shows the open mold with the part falling free.

As the parison is extruded, the melt is free to swell and sag. The process requires a viscous resin with consistent swell and sag melt properties. For a large container the machine is usually equipped with a cylinder and a piston called an accumulator. The accumulator is filled with melt from the extruder and emptied at a much faster rate to form a large parison; this minimizes the sag of the molten tube.

With a simple parison, the large-diameter sections of the bottle have a thin wall and the small-diameter sections have a thick wall. Certain modifications of



the die can control the thickness of the parison wall along its length, which results in a bottle with improved wall thickness distribution and better strength. The most common blow molding resin is HDPE used to produce containers ranging in size from 30 cm³ to 200 L.

In injection blow molding, a parison is injection molded onto a core pin; the parison is then rapidly transferred via the core pin to a blow mold, where it is blown by air into an article. This process is applied to small and intricate bottles.

Soft-drink bottles made from PET are usually made by stretch-blow molding in a two-step process. First, a test-tube-shaped preform is molded, which is then reheated to just above its glass-transition temperature, stretched, and blown. Stretching the PET produces biaxial orientation, which improves transparency, strength, and toughness of the bottle. A one-step process is used for many custom containers that are injection stretch-blow molded.

Development—trends in blow molding focus on the optimization of the viscoelastic properties and improvement in thermal stability of polymers other than HDPE to develop new extrusion-injection blow molding grades; fabrication of small containers by multilayer blow molding for improved barrier properties to water, oxygen or hydrocarbons; prediction through software packages of wall thickness for parisons and final parts to minimize materials usage.

4.2. Rotational Molding. Hollow articles and large, complex shapes are made by rotational molding, usually from polyethylene powder of relatively low viscosity (64–66). The resin is in the form of a fine powder. A measured quantity is placed inside an aluminum mold and the mold is heated in an oven and rotated at low speed. The resin sinters and fuses, coating the inside of the mold. The mold is then cooled by water spray and the part solidifies, duplicating the inside of the mold.

A rotomolding machine has three long arms extending from a central driving mechanism; each arm rotates several molds in two planes. The arms are moved from one process station to the next, ie, from unloading and loading to heating and cooling. Tooling costs are low. The molds are usually made of cast aluminum, but sheet metal is also used. The melt is forced without pressure against the mold surface during heating or cooling, resulting in uniform wall thickness, zero orientation, and high physical properties. Cycle times are long because of the heating and cooling required; they depend on wall thickness and can be as high as 15 min for a 4-mm wall thickness. Common rotomolded products include large tanks and boxes, drums, furniture, and toys. The PVC plastisol, a mixture of fine PVC particles and a plasticizer, may also be processed by rotomolding. Plastisols are liquid at room temperature and are converted to soft solids when heated to ca 180°C. Playballs and toys are made from plastisols.

Among recent trends and developments in rotomolding are the use of microprocessors and temperature sensors for quality assurance, the refinement of methods to produce multiwalled solid or foamed structures all coupled with the continuing availability of new resin grades with suitable viscosities and high thermo oxidative stability over the prolonged periods of time in the oven.

4.3. Expandable Polystyrene Molding. Molding expandable polystyrene gives foamed products such as insulation board shapes for packaging and disposable food and cup containers. Such processes are also called bead or steam molding (67,68). Expandable polystyrene moldings are manufactured

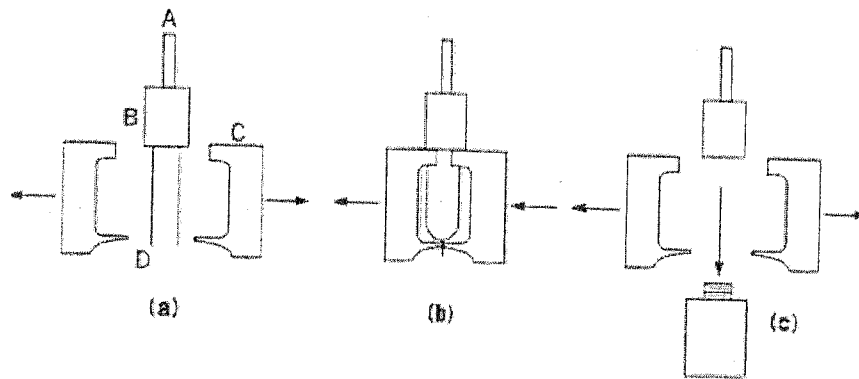


Fig. 15. Three stages of blow molding (a-c): A, air line; B, die; C, mold; and D, parison. See text.

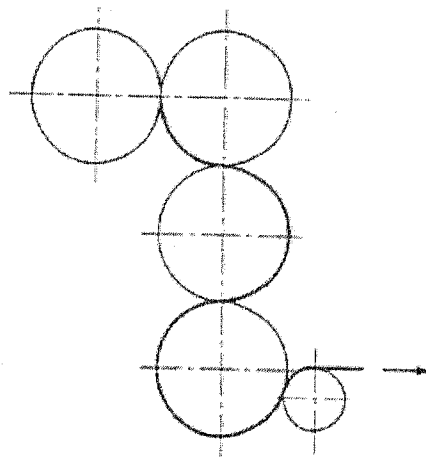


Fig. 16. A four-roll, inverted "L" calender.

3.5. Blown Film. The blown film process (Fig. 6) uses a tubular die from which the extrudate expands in diameter while traveling upward to a film tower. The top of the tower has a collapsing frame followed by guide and pull rolls to transport the collapsed film to subsequent slitting and windup rolls. The tubular bubble from the die is inflated to the desired diameter by air passing through the center of the die. Although primary cooling to solidify the melt is supplied by an external air ring, chilled air may also be used internally. Polyethylene is the primary plastic used in most films, especially for packaging and trash bags. Coaxial dies can be used for manufacture of coextruded multilayer films.

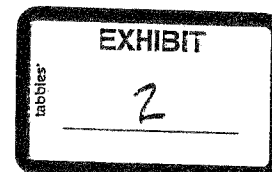
The tube is characterized by its blow-up ratio, ie, a larger diameter than the die opening, which is expressed as the ratio of bubble diameter to the die diameter. Typical blow-up ratios range from 2:1 to 4:1. The final film thickness is much thinner than the die gap. Die gaps are slits of ~ 0.65 mm. Typical film thicknesses are 0.007–0.125 mm. The process requires a high melt viscosity resin so that the melt can be pulled from the die in an upward direction. Since only air is used for cooling, removal of heat tends to be slow and rate limiting. Chilled air can also be used internally to improve the efficiency of the air cooling process. The film may be treated for subsequent printing, and it can be slit into various widths and wound onto separate cores.

3.6. Cast Film. The cast film process provides a film with gloss and sparkle and can be used with various resins. Figure 7 is an illustration of the essential features of the extrusion equipment. The die opening is a long straight slit with an adjustable gap ~ 0.4 mm wide. The die is positioned carefully with respect to the casting roll. The casting or chill roll is highly polished and plated and imparts a smooth and virtually flawless surface to the film. The roll is cooled by rapid circulation of water. Temperature control is critical. A die somewhat longer than the width of the film is needed, because the molten web becomes narrower as it is drawn from the die; this is called neck-in. Edges of the film thicken and are mechanically removed before the film is wound on a roll. The edge trim can be reprocessed.

One of the requirements of this process is that the melt maintain good contact with the chill roll, ie, air must not pass between the film and the roll. Otherwise, air insulates the plastic and causes it to cool at a rate different from the rest of the plastic and this spoils the appearance of an otherwise satisfactory product. The melt should not emit volatiles, which condense on the chill roll, reduce heat transfer, and mar the film's appearance. The cast film process allows the use of a higher melt temperature than is characteristic of the blown film process. The higher temperature imparts better optical properties.

Film stretching is a process to impart biaxial orientation in the film by stretching it in two directions simultaneously, the transverse and machine directions, respectively. The process is carried out in a device that grips the edges of the film and extends them to larger widths as the film moves from the inlet to the exit roller. The objective is to increase the modulus and strength of the film uniformly along the entire film plane. Both PP and PET have been used successfully in this process (37).

3.7. Sheet. The process used to make an extruded plastic sheet is illustrated in Figure 8. Sheet thicknesses are 0.25–5 mm and widths are as great as 3 m. Heavier gauge sheets are usually cut to a specified length and



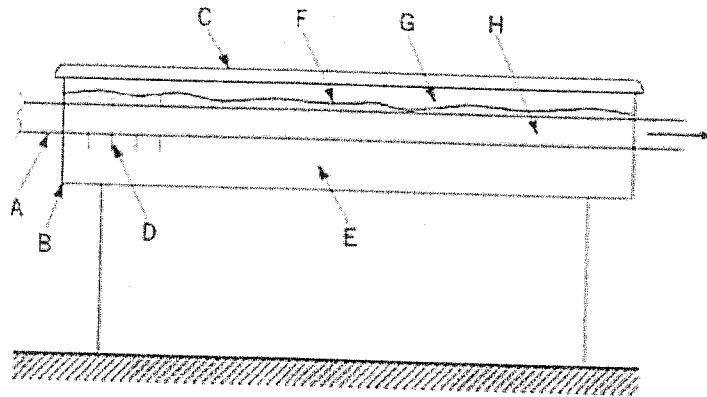


Fig. 5. Vacuum calibrator for pipe and tubing extrusion: A, molten tube from die; B, tank; C, hinged cover with gasket; D, sizing rings; E, circulated and temperature controlled water; F, water level; G, vacuum; and H, inside of pipe open to atmospheric pressure (20).

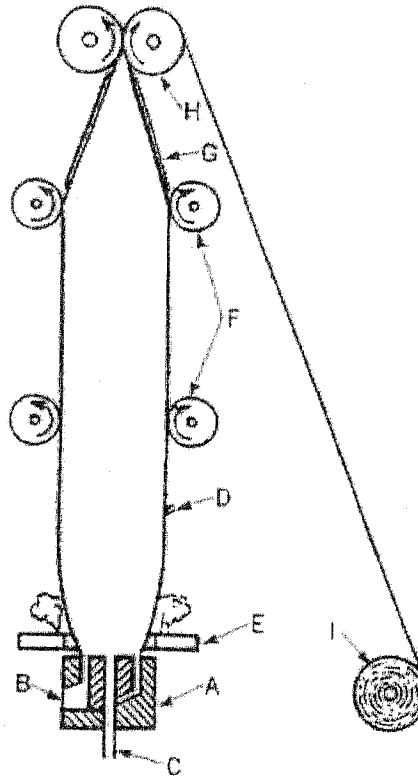


Fig. 6. Extrusion of blown film: A, blown-film die; B, die inlet; C, air hole and valve; D, plastic tube (bubble); E, air ring for cooling; F, guide rolls; G, collapsing frame; H, pull rolls; and I, windup roll (20).

[54] BLOWN FILM PROCESS

[75] Inventor: Carl B. Havens, Fresno, Calif.

[73] Assignee: The Dow Chemical Company,
Midland, Mich.

[21] Appl. No.: 710,984

[22] Filed: Aug. 2, 1976

Related U.S. Application Data

[63] Continuation of Ser. No. 554,951, Mar. 3, 1975,
abandoned, which is a continuation of Ser. No.
376,834, Jul. 5, 1973, abandoned.

[51] Int. Cl.² B29F 3/08
[52] U.S. Cl. 264/40.6; 264/95;
264/237; 425/143; 425/326.1
[58] Field of Search 264/89, 95, 210 R, 237,
264/40.1, 348, 40.6; 425/143, 170, 72, 326 R,
326.1

[56] References Cited

U.S. PATENT DOCUMENTS

3,092,874 6/1963 Fallwell 264/40.1
3,125,616 3/1964 Cook et al. 264/40.1

OTHER PUBLICATIONS

Film Cooling & Frost Line-Polyethylene Film Extrusion-An Operating Manual - U.S.I.-1960-Nat. Dist. & Chem. Corp. pp. 27-30.

"Effect of Extrusion Variables on the Fundamental Properties of Tubular Film"-Plastics, 4-1961 -vol. 26 -Clegg - pp. 114-116.

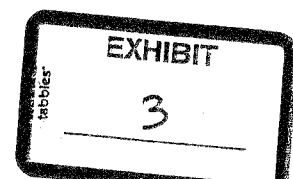
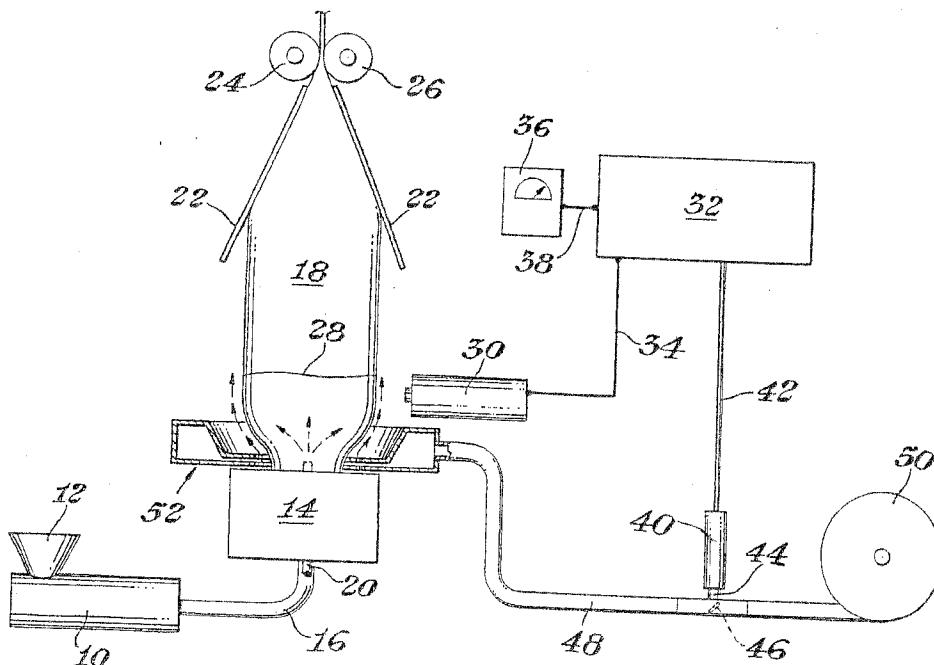
Primary Examiner-Jeffery R. Thurlow
Attorney, Agent, or Firm-Burke M. Halldorson;
Tai-Sam Choo

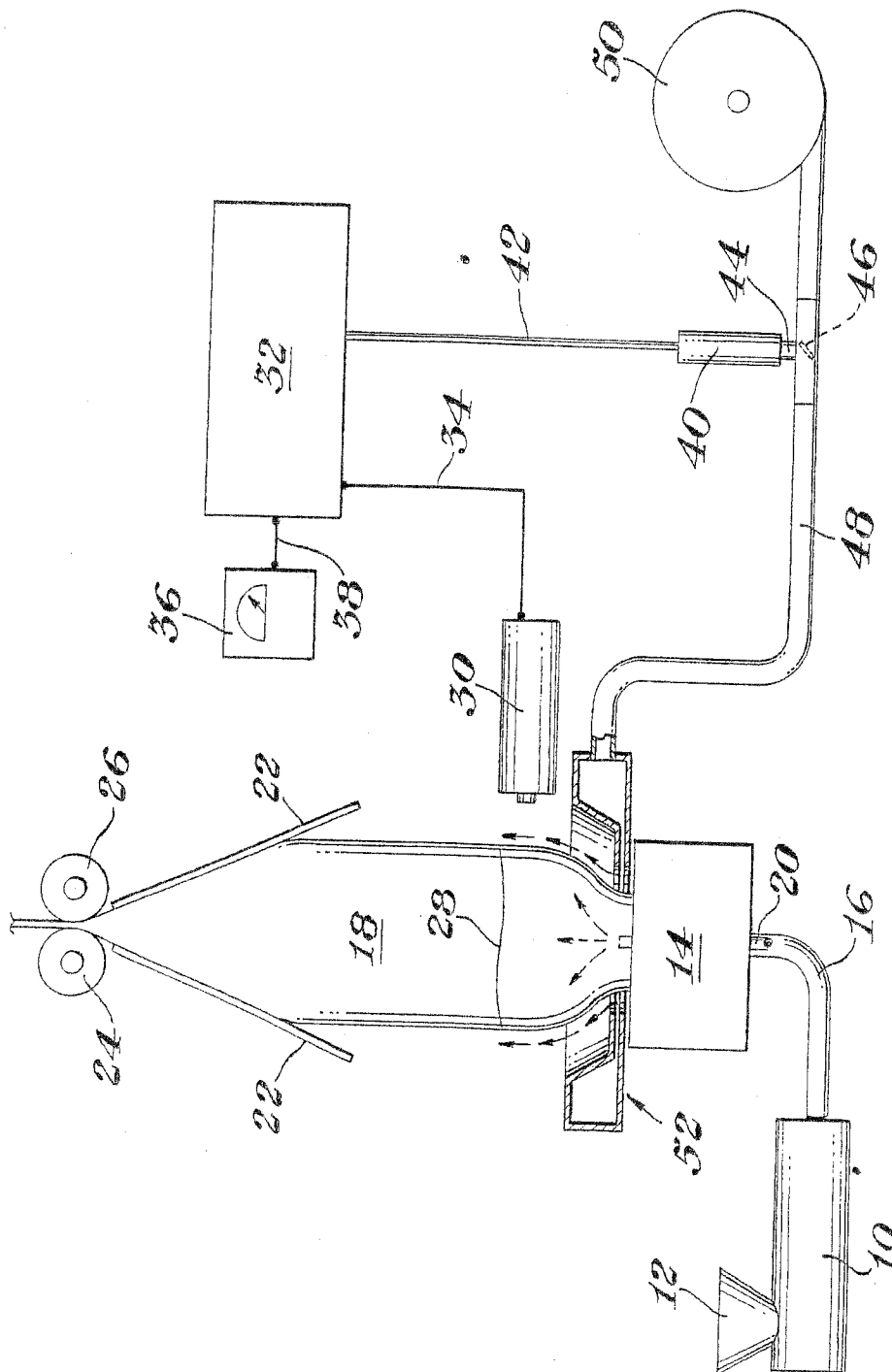
[57]

ABSTRACT

A blown film process wherein: the temperature of the film is continually monitored in a select control or target area that is remote from the film frost line; a control of "target temperature" is determined based empirically or otherwise on a given set of companion operating conditions; and a variable film cooling source or supply is regulated to establish the control temperature as an essentially constant or non-variable operating condition. The process is characterized by an essentially stable frost line position and to the extent movement of the frost line can be optically or otherwise observed or sensed, and an appropriate signal derived therefrom, the process can be alternately practiced based on monitoring the position of the frost line, defining a control or "target" frost line position, and regulating a film cooling source responsive to deviances or movement from the control position.

2 Claims, 1 Drawing Figure





BLOWN FILM PROCESS

This application is a continuation of prior application Ser. No. 554,951, filed Mar. 3, 1975, now abandoned, and which is a continuation of application Ser. No. 376,834, filed July 5, 1973, now abandoned.

FIELD OF THE INVENTION

The blown film process as expressed or intended herein, is meant to refer broadly to the manufacture of plastic film (including sheet materials) through extruding a continuous molten tube of heat plastified resin, stretching or drawing the tube about a trapped air or gas bubble, and simultaneously cooling the plastic such as by external or internal cooling means. The invention particularly relates to such a process wherein a control area is defined, a control temperature determined for such area, and maintained through variable cooling steps, whereby improved film quality, and/or increased maximum production rates or ceilings are achieved. Alternately the invention concerns defining a controlled frost line position, monitoring such position, and providing a variable cooling means to correct deviations therefrom, for essentially like purposes and improved results.

BACKGROUND OF THE INVENTION

The ultimate properties and quality of blown film can be adversely affected particularly by cyclic variations in operating conditions, and by less than perfect regularity and consistency as regards the extruded resin. For example the temperature of the extrusion apparatus tends to have inherent cyclic character. Also cyclic conditions occur in conventional film cooling systems, whether based on a refrigerated source or if taken from ambient air. Additionally, film extruders frequently require a filtering system that will gradually clog with impurities, thus inducing a variable effect, particularly a change in melt index, in the resin passed through the filter. The resin itself may not be entirely consistent in quality, such as its melt index value and melt temperature.

Operating inconsistencies such of the above type can produce poor film in the sense of poor film flatness (i.e. appearance of wrinkles in the film) and poor uniformity of the gauge profile of the film. The gauge profile can be somewhat controlled by thickness measuring devices and systems, which give the operator some indication and warning when profile control is deteriorating, so that the appropriate control corrections can be made. However, when conditions go awry causing wrinkles to appear, there have not been good devices to predict this approaching condition, and to give the operator adequate warning to make appropriate corrections.

Thus even with close attention by a skilled operator, it has been difficult to control film quality above certain ceiling production rates. Even when operating within a production range considered manageable by a skilled operator, the film quality can be less than desired and less than specification tolerances, due to imprecise and inadequate control over cyclic and/or fluctuating operating conditions.

Accordingly, it would be advantageous to the art if there were available a blown film process which achieved finer and more precise control over film quality and/or properties.

It would be particularly advantageous if such a process provided a sufficient automatic counter-balancing

effect to fluctuating and/or cyclic operating conditions to permit a significant increase in the possible rate of extrusion, while retaining an acceptable level of quality in the film produced, and/or which would consistently produce better quality film.

SUMMARY OF THE INVENTION

Briefly these and other objectives of the invention are achieved in blown film process using as a base control, the monitoring of a select control area of the film, or alternately, the monitoring of the position of the film frost line. A control temperature or control frost line position is determined which reflects the condition whereby good and preferably optimum quality film is produced, as per any given set of companion operating conditions. A variable cooling source is regulated responsive to signals received from the monitoring device, to stabilize and maintain the control temperature or control position, as applies, as an essentially constant operating condition. This system control provides precise, automatic control over film properties. It is particularly advantageous in providing prompt corrective response to the approaching condition of loss of film flatness, for which there has been inadequate warning or predicting systems in the past.

DETAILED DESCRIPTION OF THE INVENTION

The accompanying drawing illustrates a blown film process wherein there is represented and practiced a preferred embodiment of the inventive teaching and principles hereof.

Referring particularly to the drawing, a film forming resin is introduced into a heated extruder 10 through a hopper entry means 12, from whence it is eventually expelled in a heat plastified condition to a die head 14 by way of a connecting pipe or conduit 16. The resin emerges from the die in the form of a continuous tube or tubular envelope 18. The tube is stretched or drawn about a trapped bubble that is maintained and replenished by a regulated pressure line 20 that introduces generally controlled amounts of air or gas internally to the tube. A collapsing rack 22, and cooperating nip rolls 24 and 26, eventually collapse and flatten the tube at an area remote from the die head. This process will also typically include drive rolls comprising or located beyond nip rolls 24 and 26, to provide a pulling force to advance the tubing from the die. The speed of the drive rolls is controlled to stretch or draw the tubing longitudinally, and this speed factor, together with other controlling factors, will determine the circumferential size of this tube (i.e., whether it is distended, drawn-down, or maintained essentially the same as extruded size). The area of stretching occurs essentially between the die head and the film frost line shown at 28. Above the frost line, the film has advanced to a solidified or semi-solidified condition.

The invention particularly concerns a temperature sensing device 30 that is focused to read and continually monitor the temperature of the film in a control or target area that is underneath frost line 28, and above die head 14. The area of the film directly adjacent the frost line is not a good predictive or control area. This is presumably because of film crystallization effects near the frost line which tend to cause a stable temperature reading, or a reading which is not adequately predictive of changing conditions for which the control process hereof is designed to correct automatically. A good

predictive control area, however, will exist at an area remote from and spaced sufficiently downwardly from the frost line so as to be less influenced (or non-influenced) by crystallization effects occurring at and in the near vicinity of the frost line.

The signal produced by the temperature sensing device, or the output of this device, is fed to a controller or controlling means 32 through an electrical lead or connection 34, and also to a temperature reading or recording instrument 36, through an electrical lead or connection 38. The temperature reading instrument converts the signal to a dial reading, thus permitting the temperature in the control area to be determined numerically at any given time in the operation.

The output of the controller, is suited to operate an air motor or valve positioner device 40, through a pneumatic line connection 42 therewith. The valve positioner is connected by a suitable linkage assembly 44 to operate and position a butterfly type valve 46. The butterfly valve is inset in a cooling air or gas line 48 which delivers air from a blower or compressor unit 50, to a cooling ring 52 that is disposed about the lower extreme or tube 18, just above die head 14.

The system depends on the selection or determination of a control or target temperature for the control area. This is most expediently determined empirically, by arriving at a given set of operating conditions that produce optimum quality film. Upon determining a set of such conditions, the temperature in the control area is read and established as the control temperature. The dial reading while not essential in running the controls, permits the operator to observe and record, if desired, the temperature in the control area. The controller is set to continually compare the signal received from the sensing device, with the control temperature, or equivalently a pre-determined control signal. If the signal would indicate the temperature in the monitored area is rising, the controller notes the difference, and directs the valve positioner 40 to proportionately move the butterfly valve to permit increased air flow to cooling ring 52, to bring the temperature in the control area downwardly to the control temperature. Alternately a temperature drop is responded to by regulating the butterfly valve to decrease the flow or output of cooling ring 52. Necessarily the null position, that is, the position the valve assumes when reading a stable temperature condition, is at a point between the extreme open and extreme closed positions of the butterfly valve.

The invention may also be practiced utilizing the height or position of the frost line as the control indicator. The monitoring device would be modified to optically or otherwise read the frost line height and produce signals indicating deviances therefrom. The control frost line position can be determined as before, that is, by operating empirically to define a given set of conditions under which quality film is produced, and defining the control position as that at which the frost line resides under such conditions. The signal provided by the monitoring device would be fed to the controller, and compared with a control signal, and corrective action taken, as required, to regulate air line 48, to thereby maintain or stabilize the control position.

The control process taught herein is applicable broadly to the production of plastic film, from film forming synthetic resin materials, based on the blown film process(s). Representative examples of films typically produced by this process are: polyethylene and known copolymers of ethylene and various other copoly-

merizing agents such as propylene, acrylic acid, ethyl acrylate, etc.; polypropylene and known copolymers thereof, film forming polyesters, polystyrene and known copolymers thereof, vinyls such as polyvinyl chloride; saran; film forming polyamides and the like.

The monitoring devices applicable for use in the invention would be heat sensing devices such as a suitable optical pyrometer or radiation thermometer, and thermal-couples or thermistors such as of the feather sensor type, applicable for delicate web materials. When the control is based on a controlled frost line position, a haze meter can be employed to read the position of the frost line, and to produce or generate a signal upon which to base or regulate the film cooling source.

The controller is preferably of the type adapted to compare the input signal from the monitoring device with a control signal, and provide an output signal that is generally proportional with the deviance, if any, of the input signal from the control signal.

The positioning device can be electrically or pneumatically driven, depending on the input signal, space available for same, valve type, and so forth. The butterfly valve shown may be replaced by numerous other regulating valve types, or other devices adapted to regulate the flow (or conceivably temperature) of the cooling gas or air supplied to the cooling ring. The blower can supply refrigerated or ambient gas or air as would be found most optimum or necessary for any given blown film process and resins. The cooling ring is necessarily in an area where it can influence the temperature of the film in the monitored area, or the height of the frost line, as applies. Most preferably the air ring is positioned generally in the area shown by the drawing. Understandably, other cooling devices can be substituted for the cooling ring shown, or employed together therewith (i.e., of the various types known to the art, such as internally positioned cooling devices).

Certain of the known blown film processes include operating modes that may necessitate some modification hereof in order to apply these teachings to such a process. For example, a revolving die head, or a revolving take-up assembly, or the like (i.e., such as to continually revolve tube 18), is oftentimes employed in the blown film process for certain resins and to produce certain end products. The process described above can and has been applied to a revolving blown film process, in a like control procedure as that described above, essentially without modification. However, under certain conditions, it may be desirable to read or monitor several control areas about a revolving tube, and/or to employ an integrator to average the temperature in the monitored area(s), and/or to regulate a cooling change only at specific intervals, such as after each complete revolution of the film, as may be found desirable or advantageous in any specific film line.

In addition to controlling the film properties or qualities explicitly mentioned above, the control temperature and/or control frost line position can also be determined to beneficially affect the more consistent attainment of film qualities such as relates to the properties of tear and impact strength, and film shrinkage characteristics. The control temperature or control frost line height, as applies, would thus be determined in regard to such properties, empirically or otherwise, to attain more consistent achievement thereof.

EXAMPLE I

The invention as described is applied to a polyethylene "revolving tube type" blown film process having a 20 inch diameter die head. An "IRCON MODLINE", non-contacting optical pyrometer or radiation thermometer, "Instrument Series 3400," is used as the instrument to sense and monitor the temperature of the film. A control area is defined that is at least about 3 inches below the frost line, and most optimally is about 9 inches below the frost line and at least about 6 inches above the die head. A control temperature of about 240° F is established. An "IRCON" proportional controller is employed, Instrument Series 3400, that receives continually the electrical output of the optical pyrometer and converts the same proportionally into a pneumatic output that controls an air piston motor having an integral butterfly valve. The latter unit or assembly is available under the trade designation "Valteck Vector One Butterfly Valve." An approximately 1500 CFM capacity blower unit is employed, and is operated at full capacity, subject to regulation only by the controlled position of the butterfly valve. The following Table I summarizes the results comparatively between control and no control situations, wherein: "Maximum Rate" refers to the maximum achievable rate possible, but not practical for commercial runs; and "Maximum Good Production" is the maximum rate at which "good" film is produced based on the qualities of acceptable film flatness and uniformity of gauge profile. The latter figures are given in lbs/hour and also 1000 lbs/month. The monthly figure reflects "down time" and other interruptions in the process.

TABLE I

Description	No Control	Control
Max. Rate-Lbs./Hr.	675	675
Max. Good Prod.-Lbs./Hr.	550	650
Max. Good Prod.-M Lbs./Mo.	380	419

EXAMPLE II

The control process hereof is also tested in a still higher volume, polyethylene blown process or produc-

tion line, employing 30 inch diameter die, the process being also of the revolving tube type. The control process and the apparatus for accomplishing the same, is essentially the same as described supra. The control temperature and control area is near the same as with Example I. Significantly increased production capacity, as compared with the "no control situation", is also demonstrated in this test, with the results being tabulated below.

TABLE II

Description	No Control	Control
Max. Rate-Lbs./Hr.	1000	1000
Max. Good Prod.-Lbs./Hr.	800	950
Max. Good Prod.-M Lbs./Mo.	439	520

What is claimed is:

1. In a blown film process wherein film is produced through extruding a continuous molten tube of a film forming heat plastified synthetic resinous material, stretching or drawing the tube about a trapped air or gas bubble, and simultaneously cooling the tube, the steps comprising: monitoring the temperature of the film in a controlled area that is positioned between the frost line and extrusion die head, the control area being remote from and spaced sufficiently downwardly from the frost line so as to be less influenced by crystallization effects, cooling the film about its circumference between the control area and extrusion die head, setting a control temperature for the control area, comparing the monitored temperature with the control temperature, increasing or decreasing the rate of said cooling step responsive to the conditions of upward or downward drift, respectively, of the monitored temperature from the control temperature, whereby the process is characterized by an essentially constant temperature in the control area irrespective of cyclic variations in the operating parameters of the process.

2. The process of claim 1 wherein said cooling step comprises the step of varying the rate of gas flow in an air ring positioned between the control area and extrusion die head.

* * * * *

50

55

60

65

Dynamics and Criteria for Bubble Instabilities in a Single Layer Film Blowing Extrusion

SEUNGOH KIM, YUNLI FANG, PIERRE G. LAFLEUR,
and PIERRE J. CARREAU*

*Ecole Polytechnique de Montréal
Département de Génie Chimique
CRASP*

*CP 6079, Succ. Centre-ville
Montreal, Quebec, H3C 3A7 Canada*

In this paper, the performance of a new in-line scanning camera system for the study of various bubble instabilities in film blowing extrusion is critically evaluated. Three commercial film-grade polyethylenes, LmPE, LLDPE and LDPE, were used to generate the bubble instabilities. Reliable and objective criteria for differentiating various bubble instabilities such as draw resonance, helicoidal instability, and frost line height instability are proposed by using the new device. Detailed dynamics of each bubble instability was carefully investigated as a function of time in a broad range of the take-up ratio (TUR), blow-up ratio (BUR) and frost line height (FLH). In addition, effects of melt temperature and mass flow rates on dynamics of the bubble instabilities are discussed. It was found that the new system could capture the main characteristics of all bubble instabilities quantitatively. It was also found that ~~magnitude and periodicity~~ of radius variation during draw resonance of LmPE decreased as TUR increased at constant FLH and BUR. This implies that the origin of draw resonance in film blowing seems to be different from that observed in fiber spinning. In the case of helicoidal instability, eccentricity, which defines the deviation of the bubble center from the die center, decreased as TUR increased. However, the bubble could not be stabilized as expected. A graphical quantification approach to determine the stable zone in the bubble stability map is also discussed.

INTRODUCTION

Film blowing extrusion converts conventional polyethylenes such as high (HDPE), linear low (LLDPE) and high-pressure low density (LDPE) polyethylenes into thin plastic films. It is one of the most important forming processes in the plastic industry. Although this process is too complicated to be completely understood because of the complex deformation kinematics and non-isothermal cooling effects, for simplicity, three important operating conditions have been frequently correlated with its performance. First, the frost line height (FLH) characterized by a formation of certain solidification zone is used as an indication of cooling effects by external air directed to the molten bubble and strongly affects the shape of bubble. Two other operating conditions to be taken into account along with FLH are the blow-up ratio (BUR) and the take-up ratio (TUR). The BUR is defined as the ratio of the final film radius (R_f) and the die radius (R_o), thus R_f/R_o .

The TUR, sometimes called the drawdown ratio, is defined as the ratio of the take-up velocity (V_f) of the nip rolls and the extrudate velocity at the die exit (V_o), V_f/V_o . Varying the speed of the nip rolls and the amount of the pressurized air inside the bubble controls the BUR and TUR, respectively. Both parameters strongly affect the thickness and final width of the film, and thus the deformation kinematics of the molten bubble. The width of the final flattened film is generally called lay-flat width in the film industry.

An ultimate goal in film blowing is to produce final film products with thin uniform gauge and good physical and optical properties at a maximum production rate. However, this is difficult to achieve because of technical restrictions. Two technical limitations related to materials have been frequently discussed in film blowing extrusion (1–4), which are presumed to have different origins: bubble instabilities and surface melt fracture (SMF, generally called sharkskin). While bubble instability can be observed even at very low flow rate owing to a mismatch of various operating conditions in film extrusion, SMF can be observed only at

*Corresponding author. E-mail: Pierre.Carreau@polymtl.ca.

EXHIBIT

APPEAL BRIEF

3

EXHIBIT

A

critical flow rates and is believed to originate from near the die exit. Thus, SMF is not directly relevant to the operating conditions of film blowing and has been the topic of a number of recent studies (5, 6).

Various types of bubble instability have been reported in the literature (7–12). Three phenomena are commonly discussed: 1) draw resonance (DR), characterized by a periodic oscillation of the bubble diameter, 2) helicoidal instability, characterized by a helicoidal motion of bubble around its axial direction and 3) FLH instability, characterized by variation in the location of FLH. Their schematic views are shown in Fig. 1. Maintaining a stable bubble during the film blowing process is a necessary condition not only for the continuous operation but also for the production of acceptable film products. Nonuniform bubble diameter results in non-uniform layflat width and thickness of the film, which diminishes its performance in the subsequent converting steps. Therefore, appearance of one of these bubble instabilities can greatly narrow the stable operating ranges of commercial productions. These restrictions on stable conditions limit not only the production rate but also the working window for producing films of good physical properties, since there is a strong interaction between processing conditions and physical properties of final films.

Han *et al.* (7, 8) were the first to present the results of bubble instabilities for a single layer film of LDPE and polystyrene (PS)/HDPE blends by recording the bubble behavior through still pictures. They observed pulsations of the bubble diameter as the stretch ratio increased under uniaxial deformation for small BUR less than unity and observed a wavy film under biaxial deformation for BUR larger than 1.5. However, it is not clear whether what they observed under biaxial stretching was the helicoidal or the FLH instability. They also argued that lowering the melt temperature

provided a more stable bubble for LDPE. Comprehensive studies of bubble instability were done by Kanai and White (9), White and Yamane (10), and Minoshima and White (11). They used LDPE, LLDPE and HDPE having different molecular structures in terms of long chain branches (LCB) and molecular weight distribution (MWD). They tackled the problem by qualitatively assessing whether or not the bubble was stable by means of visual observations at different operating conditions. They presented the data of the working space in a bubble stability map as functions of BUR, TUR and FLH with different symbols denoting stable, bubble instability (BI), meta-stable and helicoidal, which correspond to stable, DR, FLH instability and helicoidal instability, respectively. In addition, a plot of thickness reduction vs. BUR was used to assess the effect of the molecular structure on the bubble instability. However, these results were mostly qualitative, and bubble instabilities based on visual observations of the experimenter are rather subjective. Hence, a better tool has to be developed for studying bubble stability on a routine basis.

Despite the lack of detailed knowledge of the origin of various bubble instabilities, Wong *et al.* (13), Field *et al.* (14), and Micic *et al.* (15) followed the method of White *et al.*, and they compared the bubble stability of various PE's, including two metallocene PE's (13) and LDPE/LLDPE blends (14, 15). On the other hand, Fleissner (1) determined the critical drawdown speed as a criterion for the FLH instability of three high-molecular-weight HDPE's showing a different extensional rheological behavior. Obijeski and Puritt (16) used the variation of the layflat width as a criterion for classifying three instabilities such as FLH instability, DR and helicoidal instability of LDPE, LLDPE and their blends. Huang (17) used a pressure transducer to detect variations of pressure inside bubble and correlated them

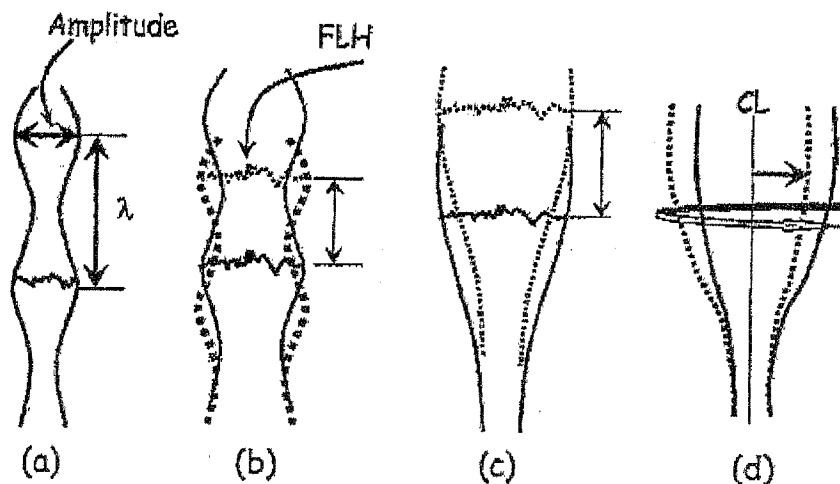


Fig. 1. Schematic views of typical bubble instabilities (a) draw resonance (DR), (b) FLH combined with DR, (c) FLH instability, (d) Helicoidal instability.

with the oscillation of various bubble instabilities. Recently, Butler (12) presented results of a comprehensive study by employing various tools: a gamma back-scatter gauge for measuring the film thickness variation in the machine direction (MD), a pressure transducer for detecting air pressure variation, a video camera for recording the layflat variation, and finally, an IR thermometer for scanning the temperature profile. However, all these methods, while useful in some cases, are indirect approaches and are not appropriate to quantitatively capture the characteristics of various bubble instabilities.

There is a strong need to develop a tool that can detect the onset of each instability and trace how it evolves as a function of time. This is a basic and necessary condition to understand the physics behind various bubble instabilities. The first quantitative approach of bubble instability was attempted by Sweeney *et al.* (18), who used a video camera along with a data analysis tool to convert the captured images on the video camera into analog voltage signal. This signal was fed to an analog filter to determine the relative positions of the bubble edges. The authors were able to capture the position of the bubble edges as a function of time and axial position, and quantify the bubble instabilities of LDPE and LLDPE blends. However, this technique is not easy to use and requires a post-data processing step to interpret the data. In addition, since a video camera was used as an image capturer, the three-dimensional motion of unstable bubbles such as encountered in helical instability could not be properly investigated.

Ghamed-Fard *et al.* (19) also attempted to quantify the bubble instabilities by defining the degree of helical instability (DHI), which takes into account the radius variation of the bubble captured by a video camera. However, they could not tell differences between various bubble instabilities, especially between helical and FLH instabilities. Recently, Laffague *et al.* (20) developed a new system using an in-line scanning camera with seven mirrors. It has been shown that it can capture all features of the bubble instabilities as a function of time and axial distance. Details of the system and preliminary results can be found elsewhere (20). However, their results were limited to the study of LLDPE, and the proposed definitions for some bubble instabilities need critical evaluation to verify their applicability to other polymers. Therefore, in this study, we have extended their work and proposed reliable criteria for various bubble instabilities in terms of experimentally determined parameters.

While many attempts at mathematical modeling have recently been made to simulate the steady-state operation of the blown film process (21–25), only a few theoretical investigations have addressed bubble instability (26–28). Yeow (26) was the first to try to predict various bubble instabilities by using a linear stability analysis for a Newtonian film under isothermal conditions. Cain and Denn (27) extended their analysis for a Newtonian and a viscoelastic upper-convected

Maxwell fluid. Cain and Denn found that both the number of steady-state solution branches and stability depended on the operating conditions represented by four variables such as axial velocity at the solidification point (V_f in their paper), amount of pressure inside bubble (A), dimensionless tension (T_p), and a parameter (B) relating inflating pressure to thickness and fluid viscosity. Based on their analysis they argued that their model can predict the draw resonance at the lower branch, i.e., lower BUR near or less than unity where the thickness and the radius of bubble decreased as the bubble moved upward. Recently Yoon and Park (28) used the mathematical approach of Cain and Denn to evaluate the detailed effects of specific operating conditions on bubble instability. They selected experimental data of LLDPE collected by Mino-shima and White (10) to assess their theoretical results based on Newtonian and isothermal conditions. It is interesting that they reported for a case of a fixed amount of air and a given thickness reduction that there was an optimum FLH that exhibited the most stable region. However, while the previous theoretical approaches are partly successful in qualitatively predicting the occurrence of DR at low BUR, none provides a reasonable agreement with all experimental observations. On the other hand, there are not enough reliable experimental data on bubble instability to form any solid consensus.

The objective of the present study was to propose reliable criteria, which can characterize quantitatively various bubble instabilities. We also present dynamics of unstable bubbles as a function of TUR and show how effective the new in-line system is in capturing the characteristics of unstable bubbles. In addition, a graphical approach is proposed to quantify the stable region in the bubble stability map. Finally, only one mass flow rate was used in previous work on bubble instability, for example 1.0 (7), 0.7 (9), 1.1 (10), 5.0 kg/h (20), which are sometimes unrealistic considering actual film blowing processes. Thus, we also discuss the effects of the mass flow rate and melt temperature on the bubble stability map.

EXPERIMENTAL

In this study the following procedure was used for all the measurements. At a given mass flow rate and a melt temperature, first the targeted BUR was attained for a given TUR by supplying the necessary amount of air, and then the targeted location of FLH was adjusted by controlling the air cooling rate. If the required BUR was attained for a certain position of FLH, then TUR was slightly varied systematically to investigate the effect of TUR while simultaneously adjusting the cooling rate in order to keep a similar FLH position. Thus, the actual BUR was not exactly the same but quite close to the targeted value as shown in Fig. 2.

Film Blowing Unit

A 45-mm Killion single-screw extruder with a standard screw was used. Its length to diameter ratio (L/D)

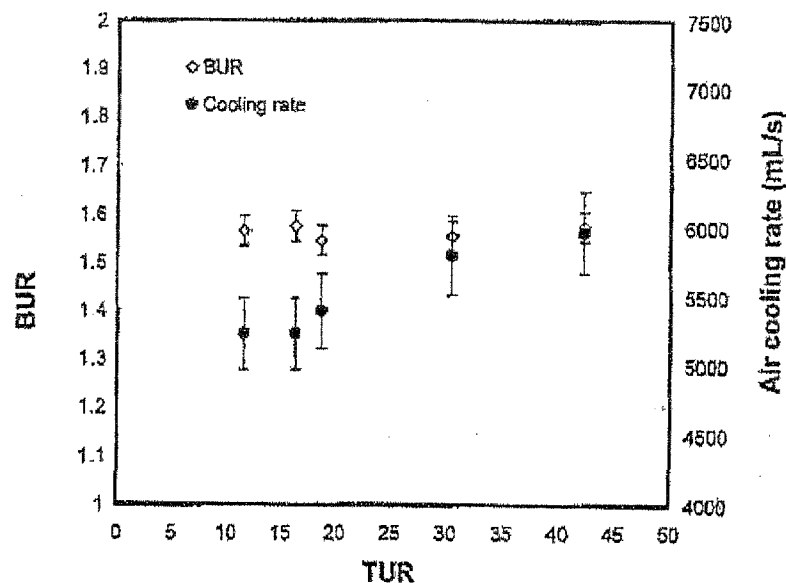


Fig. 2. Variations of BUR and air cooling rate as functions of TUR while holding an approximately constant similar FLH of 150 mm (LDPE, targeted BUR around 1.5).

is 24 and compression ratio is around 3. A helical annular die with an outer diameter of 63.5 mm and a gap of 3 mm was installed at the exit of extruder with three electrical heating bands to achieve a good temperature profile within the die. The extrusion temperature profile from the hopper to the die was set as 165/195/200/200/200/200°C regardless of the polymer used, which results in melt temperature of 184°C–187°C at the die exit depending on the polymer. The mass flow rate of each polymer was maintained at 2.0 ± 0.1 kg/h by adjusting the screw revolution speed depending on the polymer to relatively compare their bubble instabilities. However, for the evaluation of the mass flow rate and melt temperature effects on the bubble instabilities, two additional mass flow rates, 4.5 and 6.47 kg/h, and two additional melt temperatures, 204°C and 218°C, were employed with LDPE. Cooling was performed by using a dual-lip air ring, which is well known for its better cooling efficiency than that of a single-lip air ring. No internal cooling device was used. The air temperature was not regulated but was in the range of 20°C–23°C. The positions of the upper and lower lips of the air ring were set at the same level during the study to avoid any difficulty caused by variations of airflow due the lip position. Therefore, cooling of the molten bubble was controlled by an airstream mainly through the lower air ring and partly through the upper air ring. As a result, the effect of cooling was taken into account only as a function of the air-cooling rate. Typical processing data for polymers used are summarized in Table 1.

In-line Measurements

The optical system used in this study has been developed at CRASP-Ecole Polytechnique (Montreal) and the relevant mathematical derivation has been presented by Laffague *et al.* (20) in detail. The schematic view of the new system and geometrical variables of the bubble and the die are shown in Figs. 3a and b, respectively. A summary relevant to this study is given here. The system includes seven mirrors, which allow the line-scan camera (Dalsa, USA) to acquire two views of the bubble as two white stripes at the black background on the same narrow image as shown in Fig. 3a. Synchronization of the two views is a result of the symmetry of the system. Three fluorescent lamps were placed above the mirrors as a light source, and specially designed black chambers were installed around the mirrors and the camera to avoid any parasite reflections and shadows and to get optimal contrast. The whole optical system can be used at a fixed position or with a frame movable in height by using a

Table 1. Processing Conditions for a Mass Flow Rate of 2.0 kg/h.

Polymer	RPM	Torque (Amp.)	Die pressure (MPa)	Melt temp. (°C)
LDPE	9.5 ~ 9.8	8 ~ 6.5	33.1 ~ 33.8	187
LDPE	9.4 ~ 9.7	5 ~ 5.5	27.8 ~ 29.6	185
LDPE	12.4 ~ 12.7	1.5 ~ 2.0	12.4 ~ 13.1	185

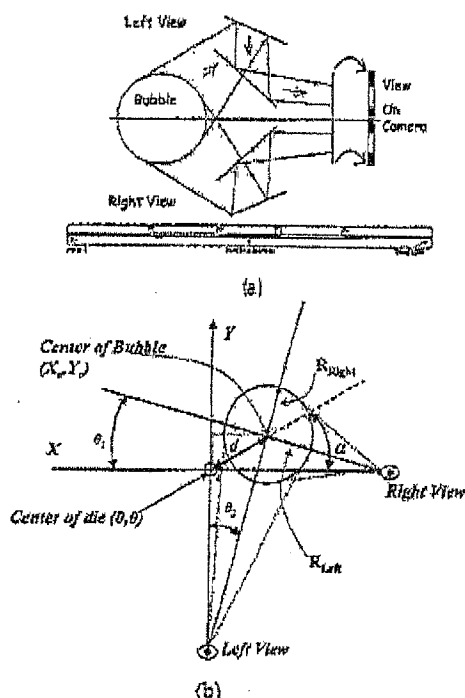


Fig. 3. Schematic view of the new system (a) and geometrical variables of bubble and die (b).

servomotor. The observations reported in this paper were made at a fixed position above FLH.

One of the important steps for successful measurements is an appropriate calibration. Through the calibration procedure, we can let the system know where the initial position of the die center is, which corresponds to the reference point of the system. In addition, there is a scaling factor to correlate the real dimensions of the bubble with the number of pixels of the data from the acquisition system. Its correlation is:

Scaling Factor:

$$\theta_1 = (P_4 + P_3)D_p/2, \theta_2 = (P_1 + P_2)D_p/2 \quad (1)$$

where P_1 – P_4 are the edge positions of two white stripes on the images of the in-line scanning camera (Fig. 3a), θ_1 and θ_2 are the angles between the bubble center and two imaginary X and Y axes (Fig. 3b), respectively, and D_p is a scaling factor.

Data-acquisition rate was fixed at 0.26 s/data point for the whole measurements, which is short enough to detect a spontaneous response of the bubble to given conditions. This system gives four parameters as output: 1) **Eccentricity**, d , describes how far a bubble moves away from the die center, 2) **Rotation angle**, α , is the reference angle of the bubble right side with respect to an arbitrary y -plane as shown in Fig. 3b, 3) **Radius** of the left and right sides of the bubble (R_{Left} and R_{Right}), and finally 4) **Ratio of the two radii**. Key

relations of these parameters and geometrical variables are presented as follows:

$$\text{Rotation angle } (\alpha) = \arctan (Y_c/X_c) \quad (2)$$

$$\text{Eccentricity } (d) = \sqrt{X_c^2 + Y_c^2} \quad (3)$$

$$\text{Radius ratio} = R_{Left}/R_{Right} \quad (4)$$

where Y_c , X_c are the Cartesian coordinates that define the bubble center.

Using these four experimentally observable parameters, we have studied the bubble instabilities as a function of time in a wide range of operating conditions. TUR was varied from 6 to 90 with a regular interval of 12 to detect any possible bubble instability. This range is broad enough to cover the typical TUR range used of 50–60 in the film industry (28, 29). However, the TUR value was slowly varied near critical conditions where a stable bubble became unstable in order to determine the precise stable/unstable transition. Within these operating conditions, LmPE and LLDPE did not exhibit any rupture behavior. However, the LDPE film bubble ruptured near TUR of 90 at the melt temperature of 186°C. The operating window for BUR was from 0.5 to 2.5. This range is slightly narrower than the typical BUR of 3 discussed in the literature (9–11). FLH was adjusted at values of 100, 180 and 250 mm from the surface of the die. These values are considered high for the size of our film-blowing unit. In addition, the variation of the air pressure inside the bubble was recorded during the study of the bubble instabilities by using a manometer mounted on the die.

Polymers Studied

Two conventional polyethylenes such as LLDPE, LDPE and a metallocene-catalyzed linear polyethylene (LmPE) were selected in order to compare their typical bubble instabilities. LDPE is made by radical polymerization and is known to possess a certain number of long chain branches (LCB) in its main backbone and relatively broad MWD. LLDPE is produced using a multi-site Ziegler-Natta (Z-N) catalyst and contains a certain weight percent of octene as a comonomer. On the other hand, LmPE, produced by using a single-site catalyst, has a narrow MWD and homogeneous short chain branch distribution. The molecular parameters for the PE's are tabulated in Table 2. Gas permeation chromatography (GPC) results in Table 2 were supplied by The Dow Chemical Co. and the ExxonMobil Company. The melt indices and densities were determined by the resin suppliers by means of the ASTM-79 and 1683 method, respectively.

CHARACTERISTICS OF VARIOUS BUBBLES

Most data discussed here were collected at melt temperature of 185°C–187°C and mass flow rate of 2.0 ± 0.1 kg/h unless otherwise stated. It is worth noting how important the duration of an experiment is for assessing bubble instability. Although this was mostly ignored in previous work, it is one of the key factors

Table 2. Molecular Parameters of Polymers Used.

Polymer	ρ (g/cm ³)	M (g/10 min)	M_n	$PI (= M_w/M_n)$	Comonomer
LDPE	0.918	1.0	111,918	2.36	C ₆
LLDPE	0.920	1.0	119,800	3.6	C ₆
LDPE	0.923	1.9	80,900	5.2	NA

when one of the processing conditions is varied near a critical point where a stable bubble becomes unstable or vice versa. Because small changes in the operating conditions near a critical condition can cause an immediate or slow response whether the bubble is stable or not, great care is needed. In this work, at least 5 min were allowed before judging the type of bubble instability. Meanwhile, all results discussed in the next section were collected at conditions away from the transition region, and the reproducibility has been verified.

A. Stable Bubble (Control)

Figures 4a–c show a typical stable bubble response recorded using the new system. These data were obtained for LDPE at BUR of 1.5, TUR of 42 and FLH of 180 mm. Figure 4a exhibits the variations of both radii as a function of time. The radii almost overlap each other, implying that the bubble is axisymmetric. This is commonly observed for a stable bubble, and the variations of both radii are in the range of $\pm 2.5\%$ of the radius as calculated by:

$$\text{Radius variation } (\Delta R) = (R_m - R_s) \times 100/R_s \quad (5)$$

where R_m is the experimentally determined radius and R_s is the set radius. A radius variation of $\pm 2.5\%$ is one of the two criteria previously proposed by Lafague *et al.* (20) for differentiating various instabilities based on experimentally determined bubble radius. This specific criterion was confirmed again in this study based on all our data collected for various operating conditions with different polymers. Figure 4b displays the variations of α and d for the same conditions as those of Fig. 4a. The variations of d describing how far the bubble center is away from the die center are within 10 mm for this polymer and all the other polymers showing a stable bubble, confirming the other criterion proposed by Lafague *et al.* (20). On the other hand, α remains within 60° , which is a typical value for most stable bubbles found in this study. Therefore, these two critical values, $d = 10$ mm and $\alpha = 60^\circ$, along with $\pm 2.5\%$ for radius variations and bubble symmetry characterized by the radius ratio, were adopted as basic criteria for differentiating various bubble instabilities. It is also worth noting that the relative difference between the maximum and minimum α is more meaningful than the absolute value, since the initial angle value is arbitrary. In addition, it is necessary to pay attention to periodic changes in α since it is generally related to the development of certain instabilities. Although variations of this angle can be dramatically reduced as the external cooling rate or TUR is decreased, they cannot be avoided because of small perturbations caused by the cooling air. Figure 4c shows

the variations of the pressure inside the bubble along with variations of α for a stable LDPE film under different conditions (BUR of 1.5, TUR of 18.6 and FLH of 180 mm). The variations of the air pressure inside the bubble are quite small, with an average pressure around 28 ± 0.4 Pa, and no periodic pattern is observed. Meanwhile, the variations of α are almost negligible in this case, since a relatively low value of TUR results in a thick film and more resistance to imposed perturbations.

B. Draw Resonance (DR)

Although the term DR originates from fiber spinning to describe the radius change of molten fibers along the stretching direction (30), similar phenomena have been reported for other processes such as cast film, extrusion coating and film blowing (3, 31). This phenomenon causes thickness variations, as we can imagine easily, owing to different expansions in the transverse direction (TD). Figure 5a shows the radius variation and the radius ratio as functions of time for LDPE when draw resonance is prevailing (BUR of 1.0, TUR of 18.6 and FLH of 100 mm). At given conditions, this phenomenon has lasted longer than 15 min. As expected, the radius variation exceeds the critical value of $\pm 2.5\%$ and reaches approximately $\pm 25\%$ with a clear periodic pattern. Meanwhile, the radius ratio is quite close to unity, implying that the bubble is still axisymmetric. Figure 5b shows the variations of α and d for the same conditions as those of Fig. 5a. Although the bubble radius is changing with a sinusoidal pattern, its center remains near the die center, d is less than 10 mm, and α shows small variations within 60° without periodicity. This phenomenon has been observed for all materials used in this study mainly at relatively low BUR near or less than 1.0 and sometimes at a large BUR of 2.0 for LDPE regardless of the FLH position, confirming previous observations (9–11). The variations of the pressure inside the bubble and the radius values collected for another time interval are presented in Fig. 5c. Both the pressure and bubble radius vary periodically and in phase, implying that the dynamics of the air inside the bubble plays a major role in this type of instability. This is in accordance with observations of Huang (17), who used a pressure transducer as a detecting device for bubble instability. The variations of the pressure are quite large for this instability, with an average pressure of 22.8 ± 1.6 Pa. The fluctuations represent about 7%, compared to 1.6% for a stable bubble. Meanwhile, as DR was frequently combined with FLH instability as illustrated in Fig. 1b, it was sometimes difficult to observe the two phenomena separately.

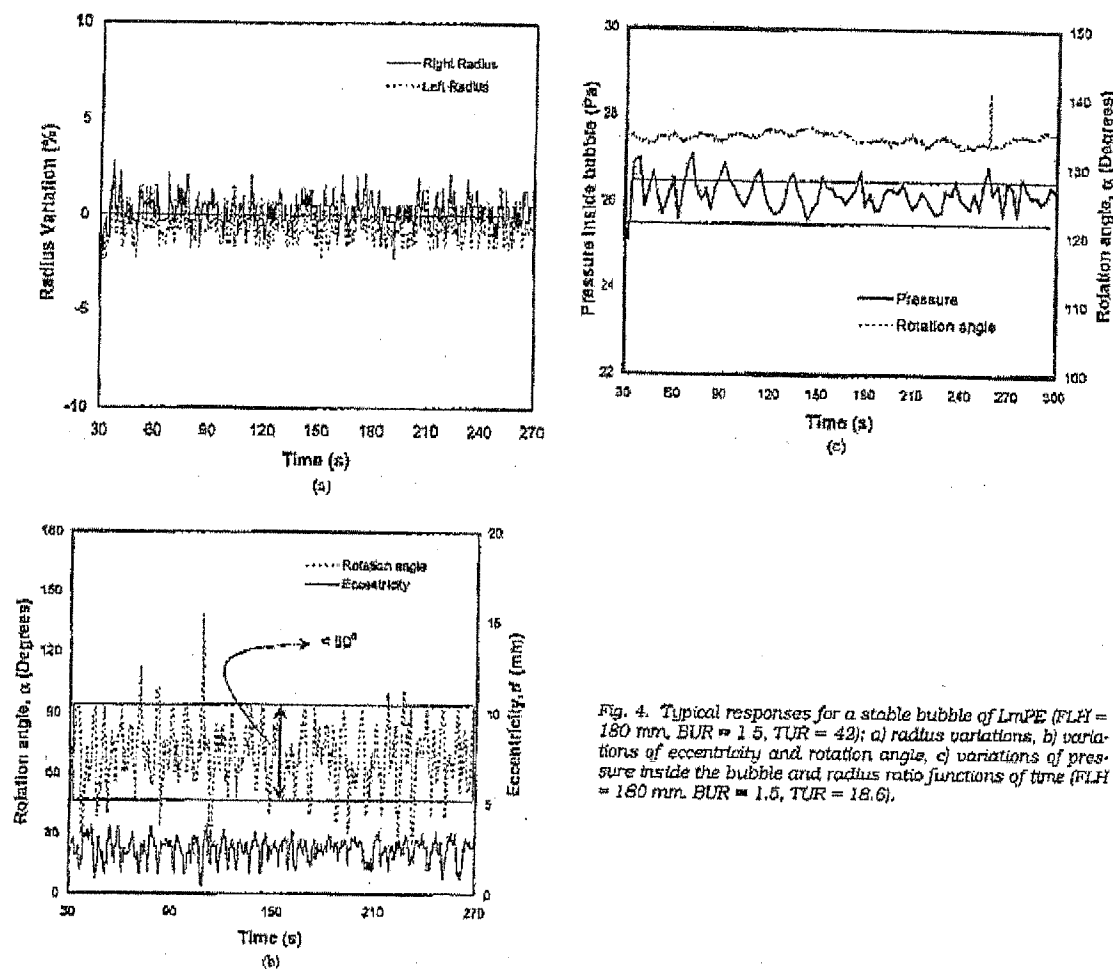


Fig. 4. Typical responses for a stable bubble of LmPE (FLH = 180 mm, BUR = 1.5, TUR = 42): a) radius variations, b) variations of eccentricity and rotation angle, c) variations of pressure inside the bubble and radius ratio functions of time (FLH = 180 mm, BUR = 1.5, TUR = 18.6).

C. Helicoidal Instability

This phenomenon has been observed for LDPE and LLDPE at relatively large values of BUR (higher than 1.5) but not for LmPE regardless of the FLH position. When this phenomenon was observed, the bubble at a position higher than the air ring was periodically rotating. Figure 6a shows α and the radius variation as functions of time for LLDPE showing helicoidal instability (BUR of 2.0, TUR of 30.5 and FLH of 180 mm). In this case, α exhibits periodic changes in the range of 0° to 360° , implying that the bubble is rotating, while the radius variation is still within $\pm 2.5\%$. Figure 6b shows the variations of the eccentricity (d) and radius ratio with time for the same conditions as in Fig. 6a. As expected, d also shows deviations from that of a stable bubble and the variations are random. However, the radius ratio is close to unity with small perturbations, implying that the bubble is still

axisymmetric. The pressure inside the bubble (data not shown) fluctuated around an average value of 33.1 ± 4.7 Pa, showing a standard deviation of around 15%, which could not be correlated well with any other parameter. On the other hand, it should be noted that this typical behavior could be observable only at moderate conditions in terms of TUR and BUR. Any change of the operating conditions in this environment could cause catastrophic changes in the bubble shape and eventually provoke the bubble collapse. It has been reported that this helical instability is associated with improper setup of the air ring (12). However, in our case, no attempt was made to adjust the air ring in order to evaluate the effects of the helicoidal instability.

D. FLH Instability

The FLH instability can be characterized by changes of the FLH position with time, and it is frequently

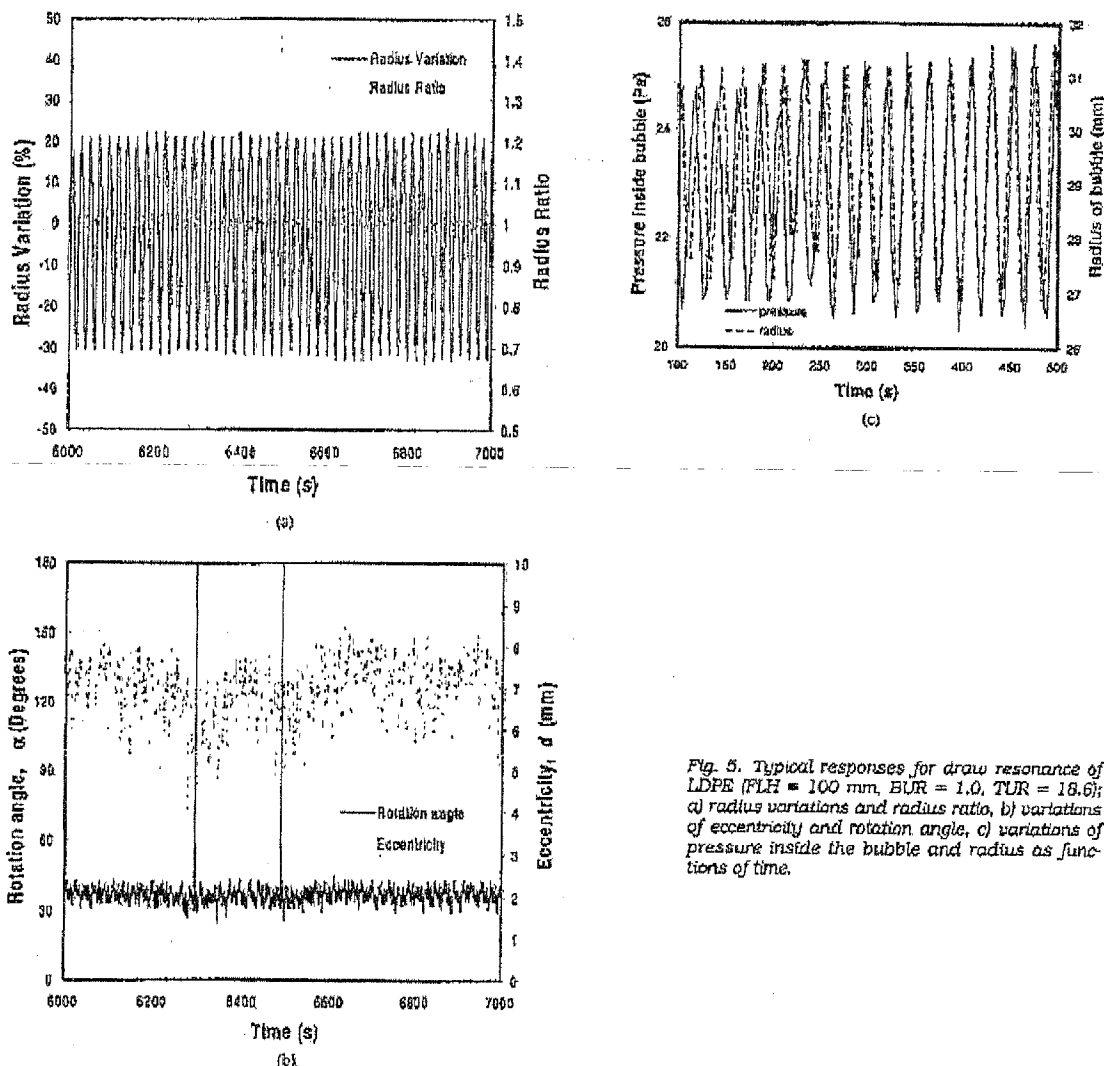


Fig. 5. Typical responses for draw resonance of LDPE (FLH = 100 mm, BUR = 1.0, TUR = 18.6): a) radius variations and radius ratio, b) variations of eccentricity and rotation angle, c) variations of pressure inside the bubble and radius as functions of time.

observed when the position of FLH is a little higher than that of the air ring. It was quite difficult to observe the FLH instability for a FLH of 100 mm in this study. For a FLH of 250 mm, BUR of 2.2 and TUR of 18.6, Fig. 7a shows how d and α respond to the FLH instability observed for LDPE. As seen in the figure, the values of d and α fluctuate around critical values of 10 mm and 60° , respectively, randomly at the beginning and then periodically near 1120–1200 s. Then, at longer times, the motion becomes random, and eventually the bubble touches the air ring at 1230 s and collapses. During the same time, the radius variation and the radius ratio reported in Fig. 7b change randomly, meaning that the shape of the bubble is not symmetric any more. Figure 7c shows the corresponding variation

of the pressure inside the bubble. A periodic pattern appears at the beginning with a long periodicity of 40 s and then periodicity is lost. Near 1230 s, the pressure drops suddenly because of the bubble collapse. The average pressure inside the bubble is around 41.6 ± 3.2 Pa and the standard deviation of 7.63% is quite close to that obtained in draw resonance. Therefore, the use of a single pressure transducer does not allow us to distinguish between FLH instability and draw resonance.

The typical FLH instability described above was also observed for LLDPE at large BUR values of 2 and 2.5, and high positions of FLH but not for LDPE. Contrary to the description made by Minoshima and White (10), all parameters vary randomly with time or sometimes

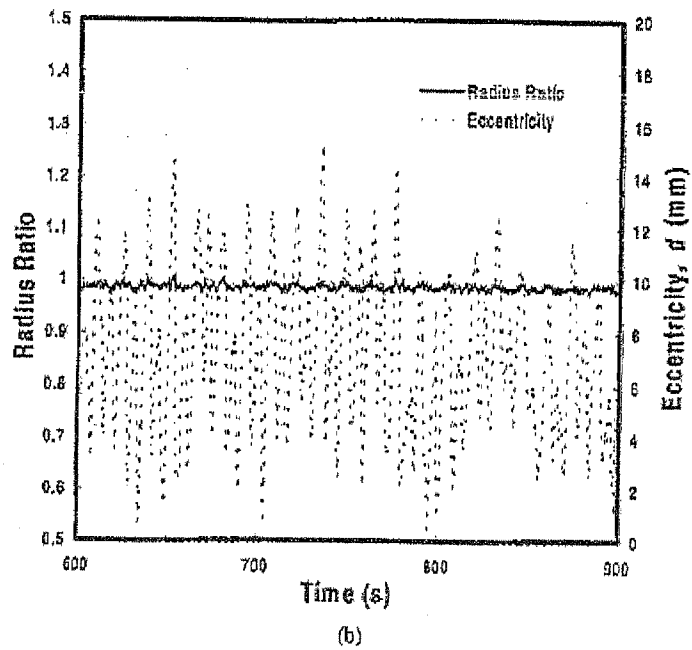
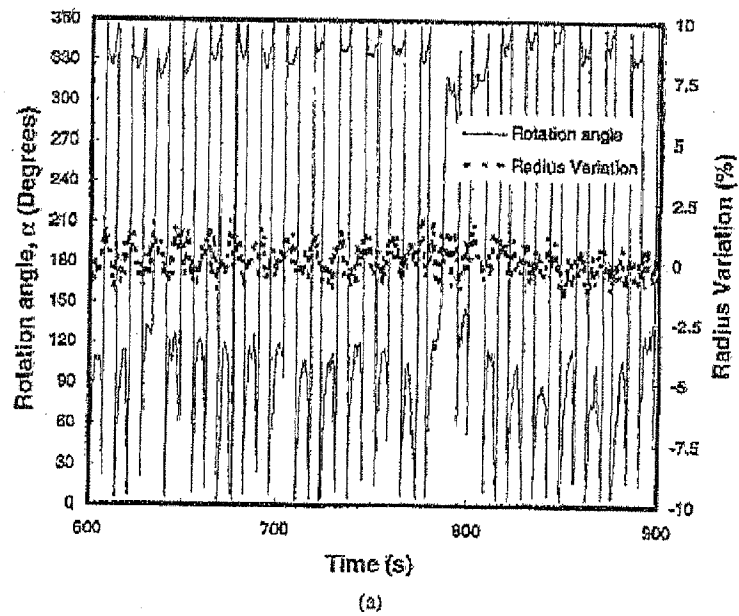


Fig. 6. Typical responses for helicoidal instability of LLDPE ($FLH = 190$ mm, $BUR = 2.0$, $TUR = 30.5$): a) radius variations and rotation angle, b) eccentricity and radius ratio as functions of time.

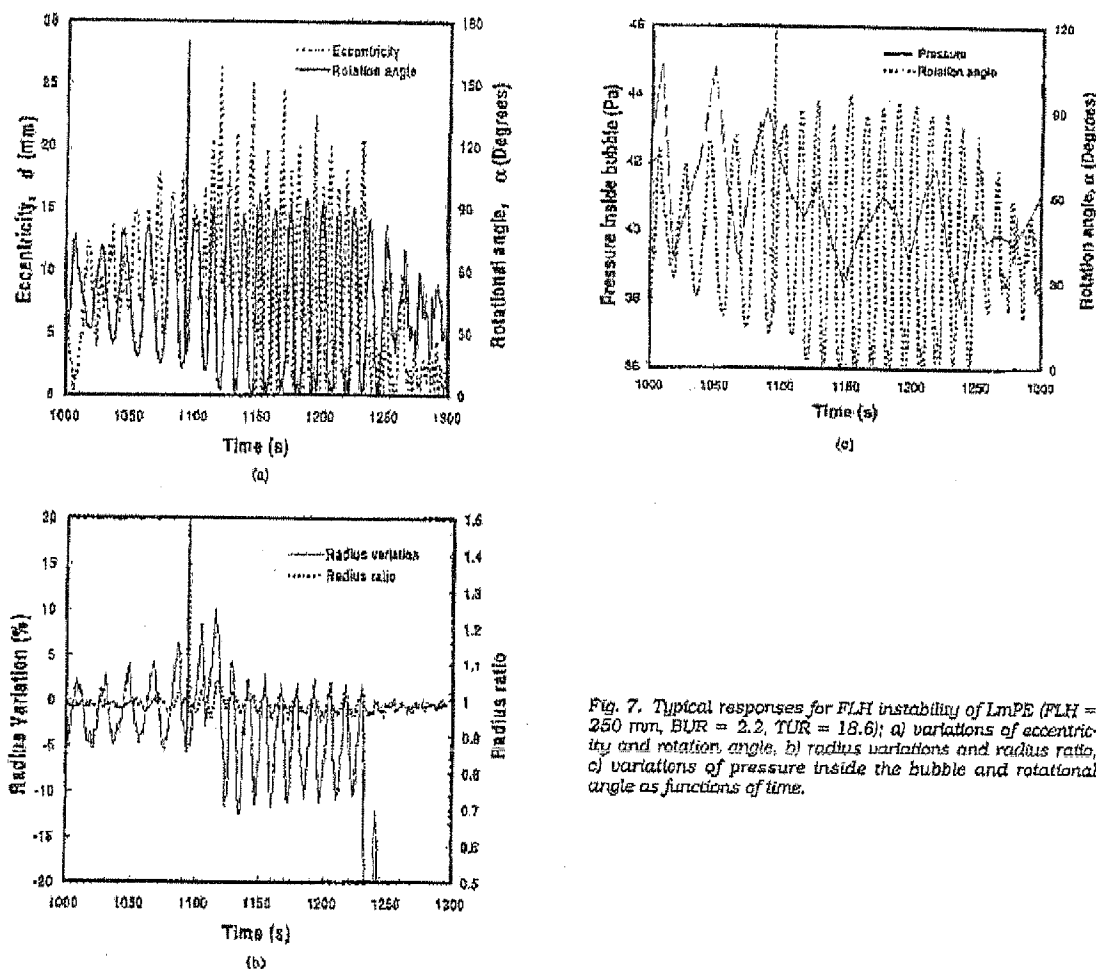


Fig. 7. Typical responses for FLH instability of LmPE (FLH = 250 mm, BUR = 2.2, TUR = 18.6): a) variations of eccentricity and rotation angle, b) radius variations and radius ratio, c) variations of pressure inside the bubble and rotational angle as functions of time.

periodically. This can be easily understood taking into account the swirling motion of air trapped inside the bubble, affected by local cooling effect at the inner and outer surfaces of the bubble. Furthermore, periodic patterns were observable only at the beginning of this instability since the bubble could not hold its shape for a long time, owing to drastic changes of FLH. Despite the lack of knowledge on the origin of this phenomenon, heterogeneous cooling effects, unstable aerodynamics inside the bubble and nonuniform crystallization behavior of given polymer melt seem to be responsible for this phenomenon. Further study is needed to understand how FLH instability develops and elucidate the causes.

E. Additional Observations

An additional bubble instability has been observed for all the polymers used in this study at the very small TUR of 6 and large BUR of 1.8–2.0. Its schematic

representation is shown in Fig. 8, and corresponding responses from the new system are shown in Fig. 9. While most previous instabilities are almost symmetric in their shape except a strong FLH instability, it is not the case for this instability, as shown in Fig. 9a. The variation of the bubble shape with time is quite different depending on the viewpoint of the experimenter (Fig. 8). Thus, visual inspection may result in a misleading judgment. When this phenomenon is observed, the initial FLH remains unchanged, whereas all parameters show deviations from those of a stable bubble. However, as time evolves, the FLH moves slowly up and down while d and α deviate from those of a stable bubble as shown in Fig. 9b. The deviations become larger and larger, and eventually the bubble touches the air ring and collapses. The reason for this behavior is not yet understood. However, we believe that this originates from a nonuniform thickness profile coupled with a nonuniform cooling rate around the air ring.

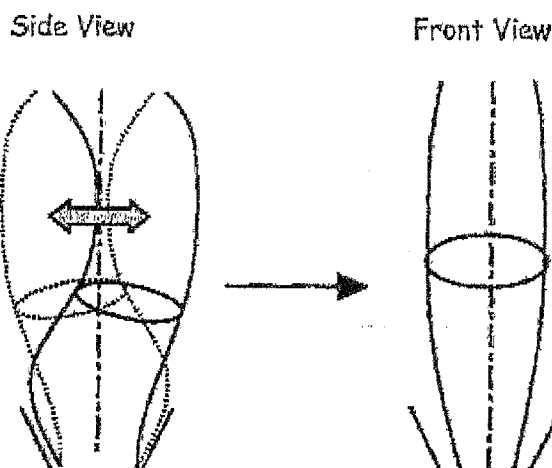


Fig. 8. Schematic views of additional bubble instability from two different points of view.

It is worth noting that although all parameters deviate from those of a stable bubble as in the case of FLH instability, all the variations are periodic, unlike those of FLH instability.

F. Proposed Criteria for Typical Bubble Instabilities

Based on the critical values for four parameters described in the previous section, we propose the criteria for differentiating the various bubble instabilities as shown in Table 3. Since the four parameters can be directly obtained from the in-line measurement and evaluated through Eqs 2–5, each bubble instability can be characterized by a combination of these four parameters, with their degree of variation denoted by two symbols, "O" and "X." The symbol "O" means that the parameter is sensitive to a given instability. For example, the four parameters can be described as "O" in the following cases: 1) the relative difference between the maximum and minimum α is greater than 60° with periodicity, 2) the value of d is larger than 10 mm, 3) the radius variation is larger than $\pm 2.5\%$, and 4) the radius ratio deviates from the unity and shows periodic changes. All the other cases can be expressed by the use of "X." Thus, a combination of all parameters should be all "X" for a stable bubble, which shows no change in all four parameters. DR can be characterized by radius variations only as expected. These criteria have been thoroughly evaluated by using three polymers under various conditions. The reproducibility of the results has also been verified.

RESULTS AND DISCUSSION

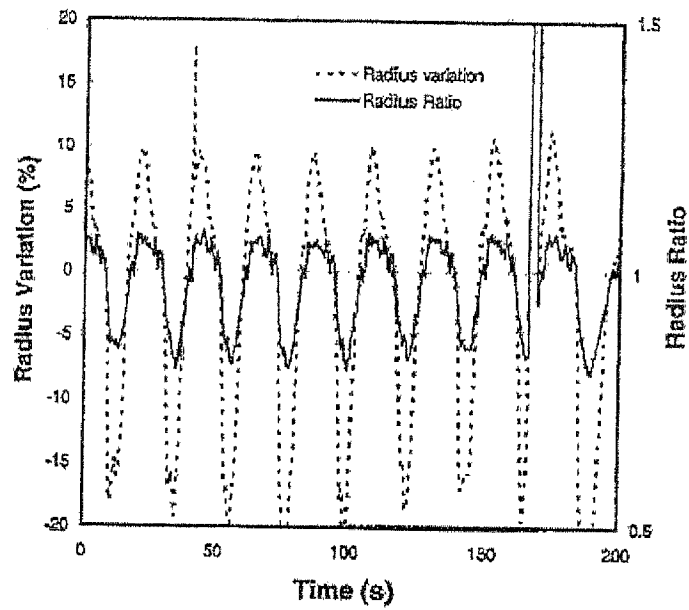
Dynamics of Unstable Bubbles

One of the advantages of the new in-line scanning camera system is that it can give very valuable information for the transition between stable and unstable

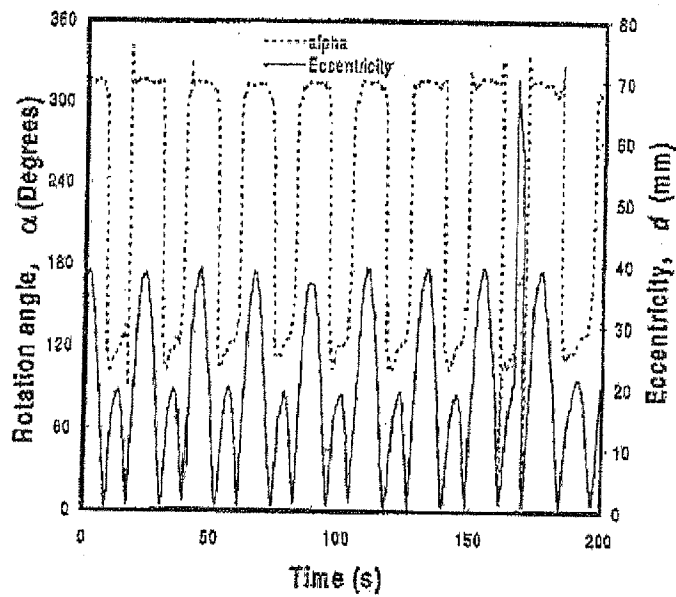
zones. This kind of information is not available in the literature. Therefore, we present some examples on how this system can capture the dynamics of an unstable bubble when it transits from unstable to stable, and vice versa.

A. Evolution of Draw Resonance at Low BUR

Figure 10 shows an evolution of draw resonance as a function of TUR for LmPE. Initially, the bubble was unstable, showing DR for the given processing conditions (BUR of 0.9, FLH of 180 mm, TUR of 6.8). Then, TUR was increased from 6.8 to 54.1 by steps of 12 and allowing a certain time interval in order to obtain a pseudo steady-state response of the bubble. As TUR increases, the radius variation is drastically reduced. Initially, the radius variation is $\pm 45\%$, but it decreases to $\pm 15\%$ at TUR of 42.3, and eventually it approaches $\pm 2.5\%$ when TUR is further increased to 54.1, which meets one of the criteria for a stable bubble. Although not presented here because of space considerations, the variations of the other parameters such as d and α are within the limits for a stable bubble. The amplitude and periodicity, denoted as λ in the Fig. 1a, are shown in Fig. 11 for this DR. The amplitude of DR was calculated simply by subtracting the set radius from the maximum radius at the given TUR. One interesting observation is that as TUR increases, the amplitude decreases to zero, which means that the bubble becomes stable. The periodicity initially decreases and then approaches a plateau different from zero. This is, in fact, a quite different behavior compared to that of DR in fiber spinning, where the amplitude of the radius variations increases as TUR increases beyond a critical value and then the fiber ruptures. Furthermore, DR in film blowing was frequently observed for a BUR of 1.0 or little larger value where the deformation kinematics is not uniaxial but planar or nonuniform biaxial, implying that the origin of this phenomenon is not the same.



(a)



(b)

Fig. 9. Responses for additional bubble instability of LmPE (FLH = 180 mm, BUR = 1.98, TUR = 18.6); a) radius variations and radius ratio, b) variations of eccentricity and rotation angle as functions of time.

Table 3. Summary of Proposed Criteria for Bubble Instabilities.

Type of instability	Alpha (α)	Eccentricity (d)	Radius variation (ΔR)	Radius ratio (R_r/R_s)
Stable	X	X	X	X
Pure DR	X	X	O	X
FLH only	O	O	O	O
Helicoidal	O	O	X	X

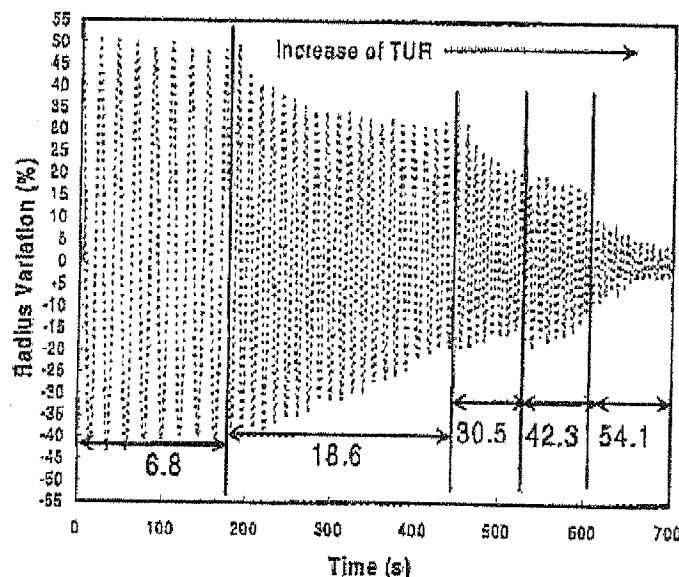
B. Evolution of Helicoidal Instability for Large BUR

Figure 12 shows an evolution of the helicoidal instability for different values of TUR in the case of LLDPE. Initially, the bubble is stable under the given processing conditions (BUR of 2.0, FLH of 180 mm and TUR of 42.3). Then, TUR is decreased from 42.3 to 18.6 in steps of 12. While changing TUR, enough time was allowed until the response of the bubble was almost independent of time, and a typical pattern was achieved. As TUR decreases from 42.3 to 30.5 as shown in the figure, the radius variation is maintained within $\pm 2.5\%$, but α starts to oscillate between 60° and 120° , implying that the bubble is rotating. Figure 13 reports the radius ratio and d as functions of time for various TUR under the same conditions as for Fig. 12. When TUR decreases from 42.3 to 30.5, the helicoidal instability appears. The shape of bubble remains axisymmetric; however, the center of the bubble is moving away from the die center. For example, d is smaller than 10 mm when TUR is 42.3, but as TUR decreases from 42.3 to 30.5 it starts to grow beyond the critical value of 10 mm. Further decreases of TUR from 30.5 to 24.5 and

to 18.6 result in larger deviations of d as well as small oscillations in the radius ratio, implying that the shape of the bubble is getting worse. Eventually, the bubble collapses because of contact with a section of the film blowing unit.

Quantification of Stable Region in Bubble Stability Map

The other issue to be resolved in a bubble instability study is how we can quantify the stable region in the bubble stability map in order to evaluate the performance of different polymers. White *et al.* (9–11) used a plot of thickness reduction of film vs. BUR. However, up to now there has been no solid method considering all effects of process conditions. Fielding *et al.* (15) and Micic *et al.* (16) recently proposed that the percent area of the stable zone within the whole working window could be used as a tool. Although this idea is good, their basis for selecting the working window is not clear enough. For this study we adopted their methodology and defined the working window as follows. Considering hardware limitations of our film unit in terms of maximum achievable TUR and BUR, a working window of TUR was selected from 6 to 90. The lower limit of TUR comes from the lowest speed of the nip rolls and the upper limit of TUR corresponds to the critical value where LDPE film ruptures. The range of BUR was selected between 0.5 and 2.5. At BUR lower than 0.5 it was difficult to produce a cylindrical bubble because of the low pressure inside the bubble. The upper limit of BUR was imposed by the air ring we used for the study since there was not enough space between the bubble outer radius and the lower lip of

Fig. 10. Evolution of draw resonance as a function of TUR of LmPE, (FLH = 100 mm, BUR = 0.9, $Q = 2.0 \pm 0.1$ kg/h, $T_{melt} = 185^\circ\text{C}$)

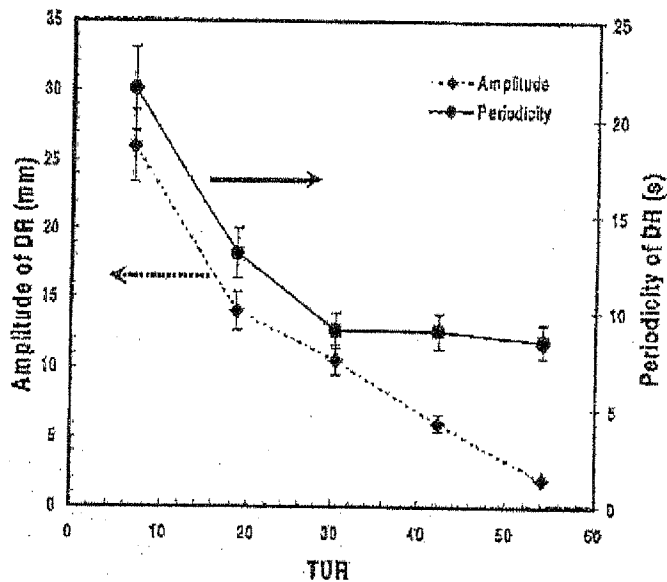


Fig. 11. Variations of amplitude and periodicity for draw resonance as functions of TUR. All conditions are the same as in Fig. 10.

the air ring, especially at FLH of 100 mm. However, much larger bubbles having BUR larger than 3 were produced at other FLH's.

Based on the proposed criteria within these operating windows, bubble stability maps were constructed for LDPE, LLDPE and LmPE at three FLH positions. Figures 14 and 15 show the bubble stability map at

FLH of 180 mm for LDPE and LLDPE, respectively. Various bubble instabilities discussed in the previous section were designated as symbols in the working windows, and a guideline for bubble rupture was placed at the high TUR region for LDPE in Fig. 14 but not for LLDPE. In addition, a critical transition zone where the stable bubble becomes unstable or vice versa as a

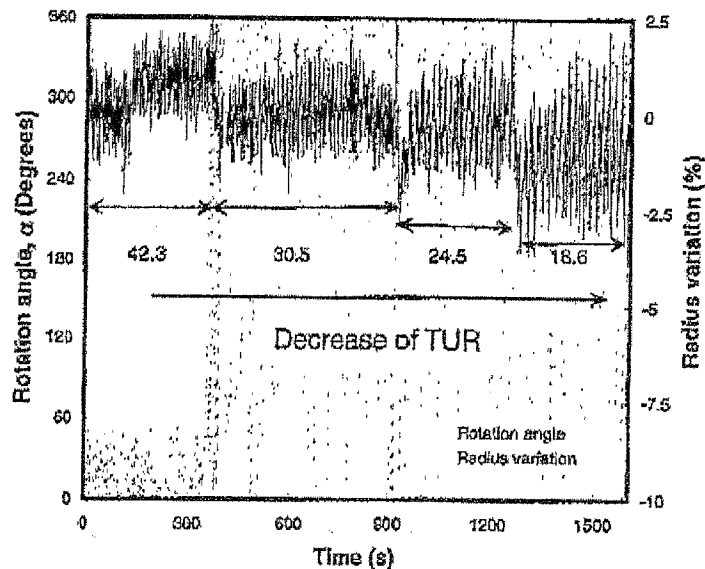


Fig. 12. Radius ratio and eccentricity as functions of time with various TUR values under helicoidal instability of LLDPE. (FLH = 180 mm, BUR = 2.0, $G = 2.0 \pm 0.1$ kg/h, $T_{melt} = 185^\circ\text{C}$.)

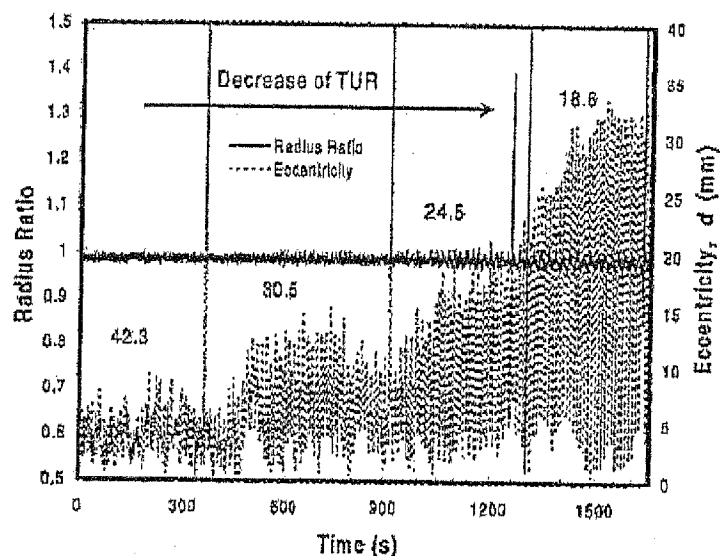


Fig. 13. Rotational angle and radius variations as functions of TUR under helicoidal instability of LLDPE. All conditions are the same as in Fig. 12.

result of changes of one of the operating conditions was found. Interestingly, the shape of the transition zone is in accordance with that predicted by Yew (26) for a Newtonian fluid, based on the experimental observations of White *et al.* (9–11) for various polyethylenes. Figure 16 shows another example of bubble stability map of LLDPE at FLH of 250 mm. The stable zone

at FLH of 250 mm is much narrower than that constructed at FLH of 180 mm (Fig. 15), implying that a more efficient cooling effect strongly stabilizes the LLDPE bubble. For quantification of the stable region, we generated small meshes in the map and calculated the shaded area corresponding to the stable region over all the area surrounded by two limits, i.e., TUR of

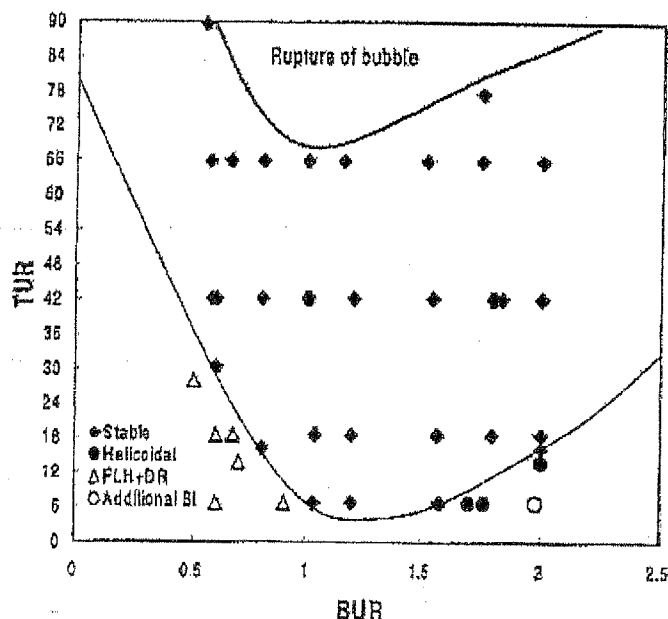


Fig. 14. Bubble stability map for LDPE as functions of BUR and TUR. (FLH = 180 mm, $\dot{Q} = 2.0 \pm 0.1$ kg/h, $T_{\text{melt}} = 185^\circ\text{C}$.)

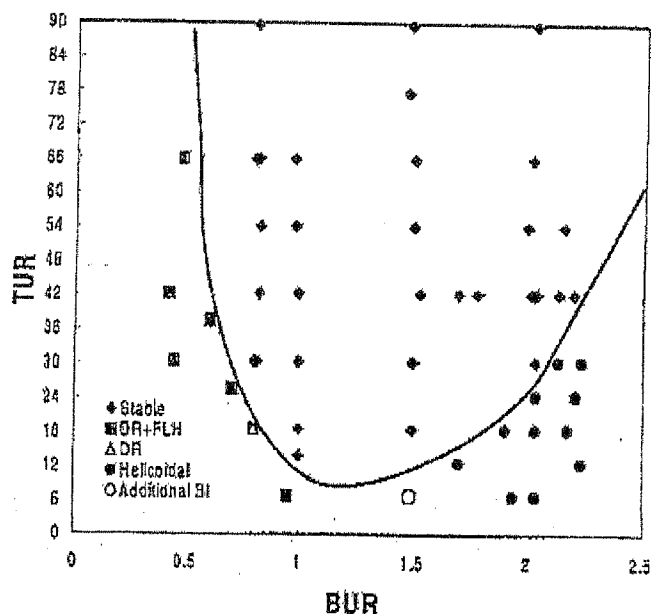


Fig. 15. Bubble stability map for LLDPE as functions of BUR and TUR. (FLH = 180 mm, $Q = 2.0 \pm 0.1$ kg/h, $T_{melt} = 186^\circ\text{C}$)

0 to 90 and BUR of 0 to 2.5, as shown in Fig. 17 for LLDPE for the same conditions as in Fig. 16. Figure 18 reports the stability order for three polymers as a function of FLH. As expected, LDPE shows the most stable

region within this working window, confirming the previous observations for LDPE (10–15). However, its stable regime increases as FLH increases, contrary to previous observations (7, 9). LLDPE shows a maximum

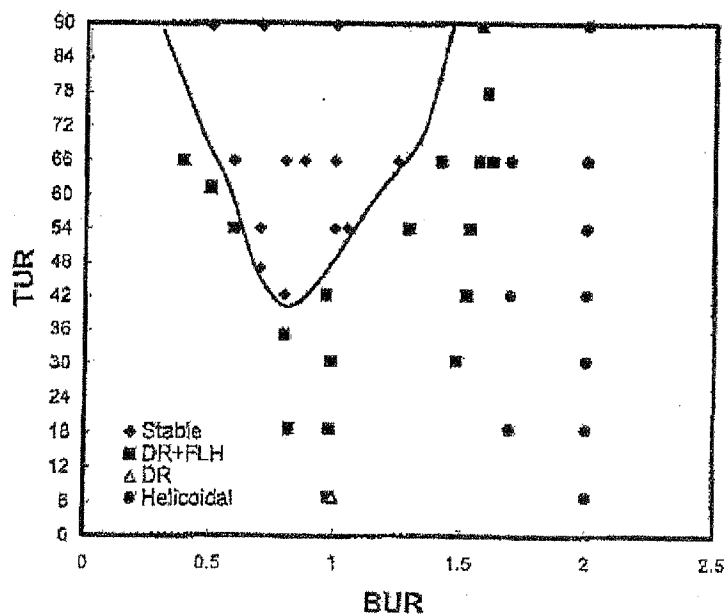


Fig. 16. Bubble stability map for LLDPE as functions of BUR and TUR. (FLH = 250 mm, $Q = 2.0 \pm 0.1$ kg/h, $T_{melt} = 187^\circ\text{C}$)

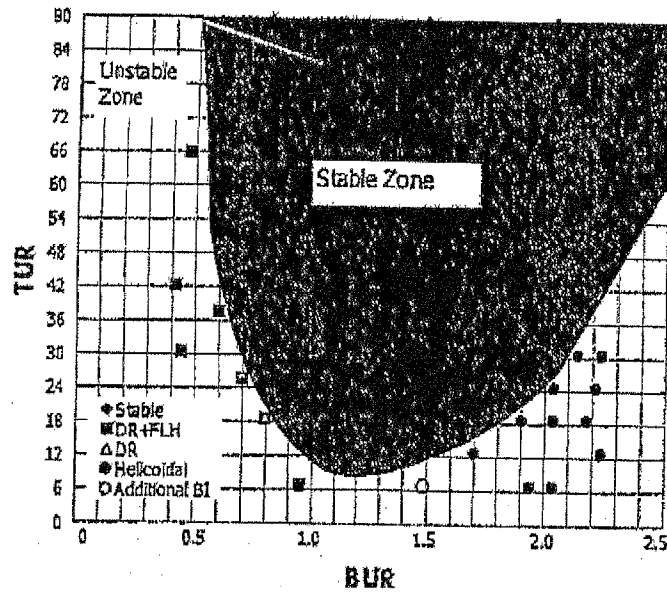


Fig. 17. Typical example of graphical quantification of stable region in the bubble stability map of LLDPE. All conditions are the same as in Fig. 15.

stable region at FLH of 180 mm, implying that there is an optimum FLH for exhibiting the best stable region, as predicted by the stability analysis of Yoon and Park (28). Finally, LmPE is the most unstable polyethylene, and its stability decreases as FLH increases.

A. Effect of Mass Flow Rate on Bubble Stability Map

Figure 19 shows the bubble stability map of LDPE for a mass flow rate of 4.5 kg/h with melt temperature of 185°C at a FLH of 250 mm. Although the extruder screw speed was varied to increase the mass

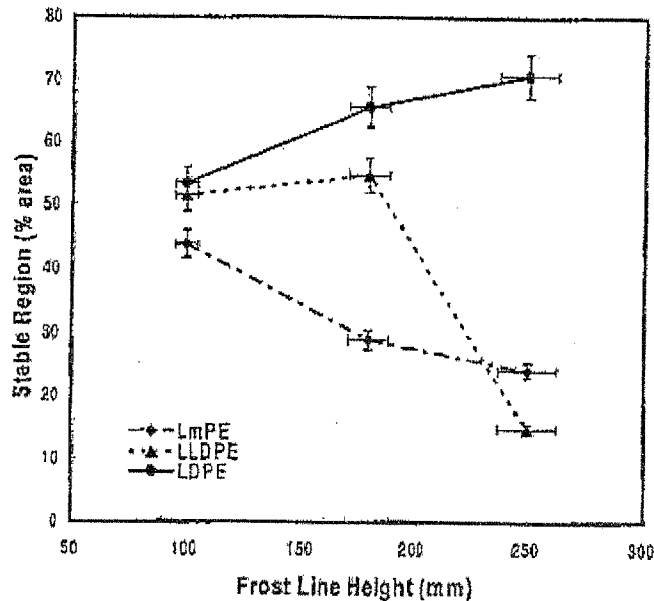


Fig. 18. Summary of bubble stability of samples used as a function of FLH. ($G = 2.0 \pm 0.1$ kg/h, $T_{melt} = 186 \sim 187^\circ\text{C}$.)

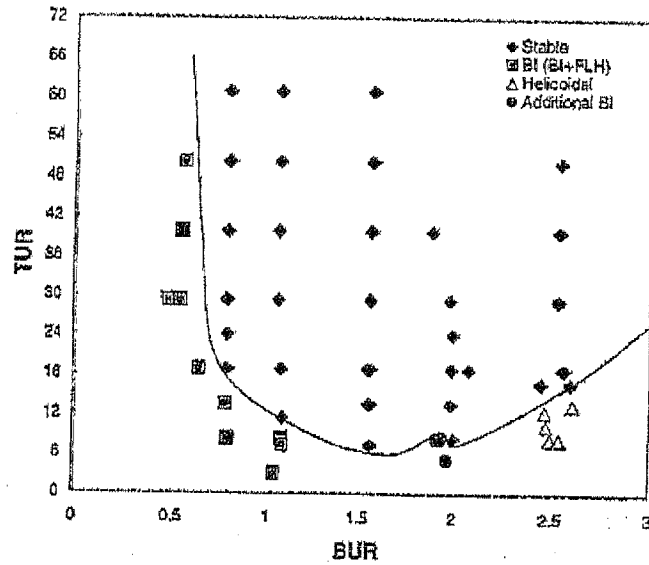


Fig. 19. Bubble stability map of LDPE as functions of BUR and TUR. (FLH = 250 mm, $Q = 4.5 \pm 0.1$ kg/h, $T_{melt} = 185^\circ\text{C}$.)

flow rate, the melt temperature increased by only 1.0–1.5°C. When the mass flow rate was increased from 2.0 to 4.5 kg/h, the general trend of bubble instability map was almost the same. I.e., the various bubble instabilities observed for a mass flow rate of 2.0 kg/h were observed at the same location in the map for the larger mass flow rate. However, the maximum

achievable TUR is decreased to 66 for 4.5 kg/h, to 38 for 6.47 kg/h, respectively, owing to an increase of the melt velocity at the die exit. Figure 20 reports the effect of the mass flow rate on the bubble stability map for LDPE. The borderline that separates the stable and unstable regions at small BUR moves drastically to the right, whereas for BUR larger than 1 it remains

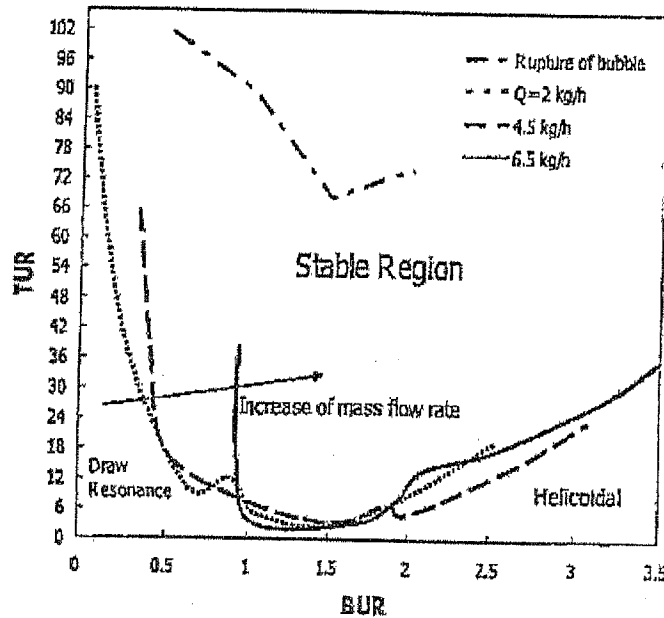


Fig. 20. Summary of bubble stability map of LDPE as a function of mass flow rate. (FLH = 250 mm, $T_{melt} = 185^\circ\text{C}$.)

about the same. This shift of the borderline to the right at small BUR seems to be related to bad cooling efficiency of air ring used for this study, since no adjustment was made to enhance its capability. In fact, it was almost impossible to make a film bubble even near BUR of 1.0 with a mass flow rate of 6.47 kg/h and under maximum cooling rate, where the film bubble could be made easily at lower mass flow rates with moderate cooling rates. We stress, however, that the use of BUR of 1 or less has no practical interest for the film blowing process.

B. Effect of Melt Temperature on Bubble Stability Map

Two additional melt temperatures were selected for this evaluation. The temperature profile of the extruder and the die was changed in order to obtain melt temperatures of 204°C and 218°C with a mass flow rate of 2.0 kg/h and a FLH of 250 mm. Figure 21 shows the typical bubble stability map for LDPE at a temperature of 204°C. Although melt temperature is increased by almost 20°C, the whole trend in the bubble stability map still remains the same as obtained for the lower temperature. However, the borderline between the stable and unstable regions is moved upward when the temperature is increased (compare Figs. 14 and 21). This trend can be seen clearly in Fig. 22, which reports the effect of the melt temperature on the bubble stability map for LDPE. The whole borderline shifts upward as the melt temperature increases from 185°C to 218°C. The rupture behavior observed for the LDPE molten film at 185°C was not observed within the experimentally attainable TUR when the temperature

was increased to 204°C and 218°C. It is possible to conclude that decreasing the melt temperature stabilizes the bubble, confirming the observations of Han *et al.* (4, 5).

CONCLUSIONS

The performance of a new in-line scanning camera system developed for the study of bubble instabilities in film blowing was critically evaluated by using LDPE, LLDPE and LmPE. Objective criteria for differentiating the various unstable bubbles are proposed based on four parameters, which can be directly determined by using the new device. It was shown that this new system could quantitatively capture the dynamics of unstable bubbles. It was also found that the amplitude and periodicity of the radius variations during draw resonance for LmPE decreased as TUR increased at a constant FLH and BUR, implying that the origin of draw resonance in film blowing is not the same phenomenon as observed in fiber spinning. Helicoidal instability and eccentricity decreased as TUR increased. However, the bubble could not be stabilized as expected. A graphical quantification approach has been proposed to determine the stable zone in the bubble stability map. The order of bubble instability can be determined based on the total percent area in BUR and TUR diagrams as a function of FLH. The order of bubble stability for the polymers used for this study is LDPE > LLDPE > LmPE. Lowering FLH stabilized the bubble for LmPEs, and it was found for LDPE that there was an optimum FLH that showed the most stable regions. The new in-line system along

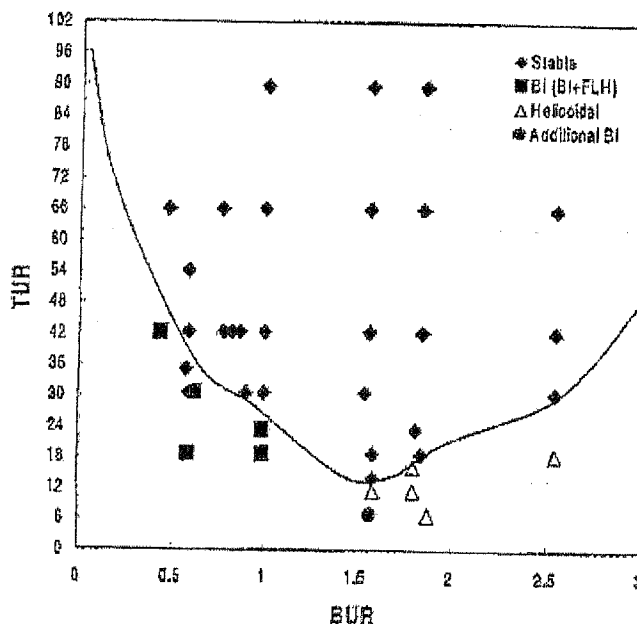


Fig. 21. Bubble stability map of LDPE as functions of BUR and TUR. (FLH = 250 mm, $\dot{Q} = 2.0 \pm 0.1$ kg/h, $T_{\text{melt}} = 204^\circ\text{C}$.)

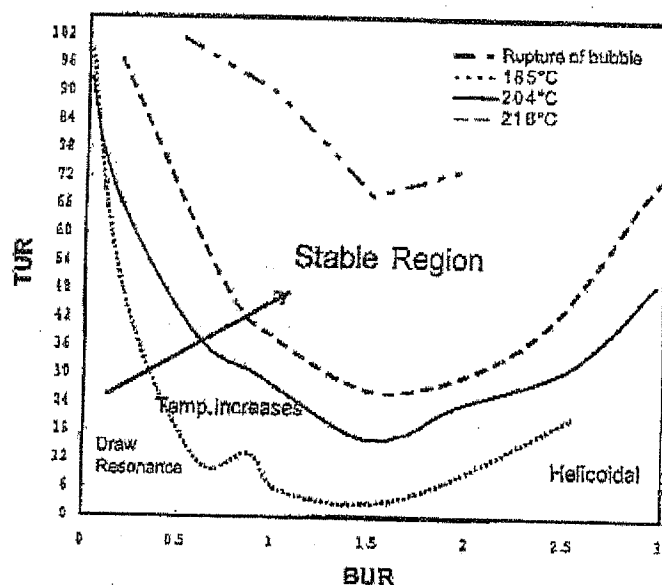


Fig. 22. Summary of bubble stability map of LDPE as a function of melt temperature. (FLH = 250 mm, $Q = 2.0 = 0.1$ kg/h)

with other tools (i.e., pressure inside bubble, infrared thermometry) is suggested for investigating the origin of bubble instability.

ACKNOWLEDGMENTS

The authors thank Dr. Willem deGroot at Dow Chemical and Mr. Thomas Sun at ExxonMobil Company for supplying GPC results of the samples. The authors extend our gratitude to Dow Chemical and ExxonMobil for supplying the samples used for this study. Finally, financial support of the National Science and Engineering Research Council of Canada (NSERC) in the form of a strategic grant is acknowledged.

REFERENCES

1. M. Fleissner, *Intern. Polym. Process.*, **2**, No. 3/4, 229 (1986).
2. A. Ghijssels, J. J. S. M. Ente, and J. Raadsen, *Intern. Polym. Process.*, **5**, 4, 284 (1990).
3. R. G. Larson, *Rheol. Acta*, **31**, 213 (1992).
4. B. Debbaut et al., *Intern. Polym. Process.*, **18**, No. 3, 262 (1999).
5. S. Q. Wang, *Advances in Polymer Science*, **138**, 229 (1999).
6. K. B. Migler, Y. Son, F. Qiao, and K. Flynn, *J. Rheology*, **46**(2), 229 (2002).
7. C. D. Han and J. Y. Park, *J. Applied Polym. Sci.*, **18**, 3291 (1975).
8. C. D. Han and R. Shetty, *Ind. Eng. Chem. Fund.*, **16**, 49 (1977).
9. T. Kanai and J. L. White, *Polym. Eng. Sci.*, **24**, 1185 (1984).
10. W. Minoshima and J. L. White, *J. Non-Newton. Fluid Mech.*, **19**, 275 (1986).
11. J. L. White and H. Yamane, *Pure & Applied Chem.*, **59**(2), 193 (1987).
12. T. I. Butler, *SPE Antec Tech. Papers*, **1**, 156 (2000).
13. T. J. Obijeski and K. R. Pruitt, *SPE Antec Tech. Papers*, **1**, 150 (1992).
14. C. M. Wong, H. H. Shih, and C. J. Huang, *J. Refrig. Plas. and Comp.*, **17**(10), 945 (1998).
15. G. J. Field, P. Micic, and S. N. Bhattacharya, *Polymer International*, **46**, 461 (1999).
16. P. Micic, S. N. Bhattacharya, and G. J. Field, *Polym. Eng. Sci.*, **38**, 1685 (1998).
17. T. A. Huang, *Advances in Polymer Technology*, **8**(1), 65 (1988).
18. P. A. Sweeney, G. A. Campbell, and F. A. Fecney, *Intern. Polym. Process.*, **7**, 229 (1992).
19. A. Ghaneh-Fard, P. J. Carreau, and P. G. Lafleur, *AIChE J.*, **42**, 1385 (1996).
20. J. Laffague, L. Parent, P. G. Lafleur, P. J. Carreau, Y. Demay, and J. F. Agassant, *Intern. Polym. Process. XVII*, 347 (2002).
21. P. P. Tas, *Doctoral thesis*, Technical University of Eindhoven (1994).
22. S. J. Kuriz, *Intern. Polym. Process.*, **10**(2), 148 (1995).
23. C.-C. Liu, D. C. Bogue, and J. E. Spruiell, *Intern. Polym. Process.*, **10**, 230 (1995b).
24. J. M. Andre, J. F. Agassant, Y. Demay, J. M. Haudin, and B. Monasse, *Intern. J. Forming Process*, **1**(2), 187 (1993).
25. A. K. Doufa and A. J. McHugh, *J. Rheology*, **43**(5), 1085 (2001).
26. Y. L. Yeow, *J. Fluid Mech.*, **75** (part 3), 577 (1976).
27. J. J. Cain and M. M. Denn, *Polym. Eng. Sci.*, **28**, 1527 (1988).
28. K. S. Yoon and C. W. Park, *Intern. Polym. Process.*, **14**(3), 342 (1999).
29. S. Milner et al., *NSF Annual Report*, "Interdisciplinary macromolecular science and engineering," Material Science Division, 48 (1998).
30. R. E. Christensen, *SPE J.*, **18**, 751 (1962).
31. C. J. S. Petrie and M. M. Denn, *AIChE J.*, **22**, 209 (1976).

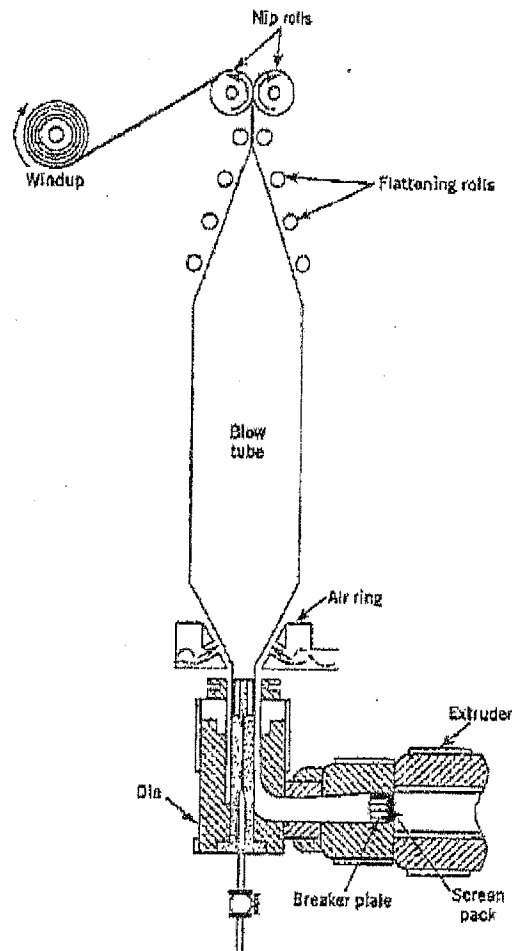


Fig. 3. Blown film extrusion.

3.1.1. Blown Film

The blown or tubular film process provides a low cost method for production of thin films (Fig. 3). In this process, the hot melt is extruded through an annular circular die either upward or downward and, less frequently, horizontally. The tube is inflated with air to a diameter determined by the desired film properties and by practical handling considerations. This may vary from as small as a centimeter to over a meter in diameter.

As the hot melt emerges from the die, the tube is expanded by air to two or three times its diameter. At the same time, the cooled air chills the web to a solid state. The degree of blowing or stretch determines the balance

EXHIBIT

APPEAL BRIEF

4

EXHIBIT

B

and level of tensile and impact properties. The point of air impingement and the velocity and temperature of the air must all be controlled to give the optimum physical properties to the film. With some polymers, an internal air cooling ring is used as well, in order to increase throughput rates and optical quality. Rapid cooling is essential to achieve the crystalline structure necessary to give clear, glossy films.

The film tube is collapsed within a V-shaped frame of rollers and is nipped at the end of the frame to trap the air within the bubble. The nip rolls also draw the film away from the die. The draw rate is controlled to balance the physical properties with the transverse properties achieved by the blow draw ratio. The tube may be wound as such or may be slit and wound as a single-film layer onto one or more rolls. The tube may also be directly processed into bags. The blown film method is used principally to produce polyethylene film. It has occasionally been used for polypropylene, poly(ethylene terephthalate), vinyls, nylon, and other polymers.

Downward extrusion of a bubble into a water bath and over an inner water-cooled mandrel is used in a few instances for polypropylene and polyesters. The water is removed prior to slitting and winding.

The double-bubble process may be used to produce biaxially oriented film, primarily polypropylene. In this process the first bubble formation is similar to the conventional blown film, except that the bubble is not collapsed. Rather it is reheated to the orientation temperature and blown and drawn further in a second stage. It is then collapsed, slit, and wound. This process is generally limited to a final film thickness of less than 24 μm .

3.1.2. Coextrusion

An increasingly popular technique to produce tailored film or sheet products is to coextrude one or more polymer types in two or more layers of melt (6). In this fashion the benefits of specific polymer types or formulations may be combined. Thus high cost barrier resins may be combined with a low cost thicker layer of standard resin to achieve an optimum barrier film at lower cost. Thin slip-control layers may be used on the surface of a bulk layer of optically clear resin to obtain an aesthetic film with good handleability. Lower melting outer layers may be used to provide heat sealing for polymers that seal with difficulty by themselves.

The layers of the different polymers or resins may be combined in one of two ways. One is to use a combining block prior to the slot extrusion die. Parallel openings within the block are fed from two or more extruders, one for each resin. The melts flow in laminar fashion through the die and onto the quench drum. The film is processed conventionally or may then be oriented. Careful control of resin viscosity must be obtained to provide smooth flow, and the resins must be compatible in order to bond together properly. The second method uses a multimanifold die to bring the melt streams together within the die. This allows use of resins with a wider difference in viscosity since fewer changes in flow patterns are necessary. Multimanifold dies may be flat or tubular. The most common types of coextrusion are AB, ABA, or ABC where A is one polymer system, B is another (of the same polymer type or different), and C is a third polymer type. Coextrusions of many, many layers lead to film products with a pearlescent appearance. Where two polymers may not adhere sufficiently, it is possible to extrude a tie or adhesive layer in the coextrusion. Ionomer resins are often used as such tie layers.

The process can be used to recover scrap or low quality resins by using them as the core layer, and using outer layers of virgin resins designed for the specific functional needs of the product such as slip or gloss and appearance. The inner core may be a foamed resin with surface layers of superior finish resins. Coextruded films often eliminate the need for costly lamination processes.

3.2. Calendering

Calendering is the process whereby a polymer is heated on hot rolls and squeezed between two or more parallel rolls into a thin web or sheet (Fig. 4) (8). The polymer is blended and masticated in preliminary operations and then fed to a rolling nip between hot, temperature-controlled rolls. The polymer mass is worked further in the nip and flows out to a uniform sheet as it passes through the nip. The web is nipped again and drawn down

DE KROON et al
Serial No. 10/511,344
April 8, 2010

X. RELATED PROCEEDINGS APPENDIX

[NOT APPLICABLE]

DE KROON et al
Serial No. 10/511,344
April 8, 2010

XI. CERTIFICATE OF SERVICE

[NOT APPLICABLE]